Persistence and Periodicity: A Study of Mendelcev's Contribution to the Foundations of Chemistry.

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PERSISTENCE AND PERIODICITY : a study of Mendeleev's contribution to the Foundations of Chemistry

by
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ABSTRACT

This thesis is concerned primarily with the characterisation and classification of the chemical elements by the Russian scientist D.I. Mendeleev (1834-1907). In connection with certain specific questions the contributions of other scientists are presented at some length in order to provide a background against which Mendeleev's work may be viewed and appraised.

Chapters I and II deal with Mendeleev's recognition of persisting entities in nature. His scientific theories were all moulded by an ontology in which the two fundamental categories of matter and motion are "infusible" but necessarily concomitant, both matter and motion being quantitatively conserved. He saw the chemical elements as the persisting invariant constituents of all simple substances and compounds, a convenient - but not necessary - model for this view being provided by his version of the atomic-molecular theory. Although Mendeleev thought it likely that the elements are complex, he came to recommend nevertheless that in the absence of any well-authenticated transmutation they should be treated pragmatically as qualitatively-distinct ultimate entities.

Chapters III-VII contain an account of the emergence and development of the periodic system of the elements. This history is then summarised and appraised in chapter VIII. The eventual construction of periodic systems in the 1860's is viewed as the culmination of various tendencies of the preceding half-century. A collection of Mendeleev's periodic tables is given; his use of the system for predictive purposes, and his approach to the problems raised by the rare-earth elements and inert gases, are considered in detail. Priority and independence of discovery of the periodic law are discussed; but in order to explain the particular impact of Mendeleev's contribution upon the scientific community more importance is attached to the degree of conviction with which the various contributions were made and to the application and development of the periodic system.

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PRELIMINARY NOTES

In connection with dates the abbreviations OS and NS are sometimes used in this thesis, denoting "old-style" (Julian) and "new-style" (Gregorian) dates respectively. The Julian calendar, which was used in Russia until 1918, ran 12 days behind the Gregorian calendar (used in Western Europe) during the 19th century, and 13 days behind in the 20th century. Where no indication of date-style is given it may be assumed that dates are Gregorian ("new-style").

Reference to works which are listed in the numbered bibliography at the end of the thesis is made by appending the abbreviation Bibl. together with the appropriate bibliography number, e.g. Kedrov, 1970 (Bibl.44).

In the text and footnotes of this thesis (but not in the bibliography) titles have often been translated into English for convenience. To indicate or emphasise the language in which a particular work was published the letter R (for Russian), G (for German), F (for French) or E (for English) is appended to the reference.

The following additional abbreviations are used -

MALU	Mendeleev archive, Leningrad University
Pr. Ch.	Principles of Chemistry (R., Bibl.65; E., Bibl.66)
Colls.	Collected works (R., Bibl.68)
Sc. Ar.	Scientific Archive. I - Periodic Law (R., Bibl.71)
PLBA	Periodic Law. Basic Articles (R., Bibl.72)
PLSM	Periodic Law. Supplementary Material (R., Bibl.74).

The various editions of Principles of Chemistry (R., E.) are designated as illustrated in the following examples: the 3rd (1877) Russian edition is referred to as Pr. Ch., R-3 (1877); and the 3rd English edition as Pr. Ch., E-3 (1905; from R-7, 1902-3).

Unless indicated otherwise, all translations from Russian in this thesis are by the present author.

CONTENTS

Drawing of Mendeleev by M.A.Vrubel', 1885.

D.I. MENDELEEV : general biographical introduction.[1]

Dmitrii Ivanovich Mendeleev was born in Tobol'sk, Western Siberia, on 27th January (O.S.) 1834, the last of the many children[2] of Maria Dmitrievna Mendeleeva (née Kornil'eva) and Ivan Pavlovich Mendeleev.

Later in the year of Dmitrii's birth Ivan Pavlovich became blind in both eyes as a result of cataracts, causing him to lose his post as director of the gymnasium in Tobol'sk[3]. Although Ivan was awarded a pension by the state this was quite inadequate for supporting his large family, which now became dependent upon the mother for its welfare.[4] To enable her to fulfil this new responsibility, Maria Dmitrievna accepted a proposal from her brother that she should take over the management of a small glass factory owned by him in the village of Aremzianka, about 25 versts from Tobol'sk[5]. The family moved to Aremzianka, where they lived until 1841. By 1841 the time had come for the two youngest children, Pavel (aged 9) and Dmitrii (7), to go to school; they entered the Tobol'sk gymnasium, and the family moved back to Tobol'sk. Maria Dmitrievna continued to run the factory at Aremzianka however, travelling to work from Tobol'sk.

At the gymnasium in Tobol'sk Dmitrii Ivanovich studied many subjects, including mathematics, physics, history, Latin, German, French and law. He was good at mathematics, physics and history, but obtained poor marks for Latin, a subject he disliked. Apart from his formal schooling, a second

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[1]The most detailed biographical sources for the early part of Mendeleev's life are Gubkina, 1908 (Bibl.25) and Mladentsev and Tishchenko, 1938 (Bibl.82). A very good biography in English of the young Mendeleev is to be found in Almgren, 1968 (Bibl.5). Biographies which cover the whole of Mendeleev's life include those in Russian by Chugaev, 1924 (Bibl.13), Pisarzhevskii, 1954 (Bibl.93) and Figurovskii, 1961 (Bibl.23); in German by Walden, 1908 (Bibl.128); in French by Kolodkine, 1963 (Bibl.49); and in English by Tilden, 1909 (Bibl.114), Posin, 1948 (Bibl.94) and Leicester, 1961 (Bibl.58).

[2]Mendeleev himself claimed that in his family there were "17 children in all, and 14 live-christened (zhivokreshchennykh)" (written 1906: see Colls., 25, 669). However, Mendeleev's mother in one of her letters says "I bore 14 children" (see Gubkina, Bibl.25, p.36).

[3]Ivan Pavlovich taught philosophy, fine arts and political economy (see Chugaev, Bibl.13).

[4]Ivan's sight was partially restored by an operation in 1837, but he did not return to full-time work.

[5]A verst measured 3,500 feet - or just over one kilometre.

important formative influence upon Dmitrii at this time seems to have been his contact with the Decembrists who were in exile in Tobol'sk[6]. A number of these (- including M.A. Fonvizin, P.N. Svistunov, I.A. Annenkov, and one of the members of the Murav'ev family) - were frequent visitors to the Mendeleev household[7]. The Russian scholar and revolutionary N.A. Morozov has subsequently written (1907), "It is to the influence of the Decembrists, as told me by the widow of D.I. [Mendeleev], that we must chiefly attribute that affection of Mendeleev towards the investigation of nature which later led him to the discovery of the 'natural system of the chemical elements'."[8]

In 1849 Mendeleev completed his schooling at the Tobol'sk gymnasium. The best pupils from the gymnasium were awarded state grants to attend university; but Mendeleev was not one of those recommended for such an award, because although he had shown exceptional ability in certain subjects, he was considered to have been somewhat lacking in application. His mother, however, was determined that he should receive higher education; and no longer having any special reason for remaining in Tobol'sk (Ivan Pavlovich had died in 1847; the glass factory had been destroyed by fire in 1848; and her other sons were now working) Maria Dmitrievna settled her affairs and set off for Moscow with Dmitrii and his sister Elizaveta, in order to get her son accepted for entry to Moscow University. But despite assistance from her influential brother, Maria failed in this attempt. Dmitrii was refused entry on the grounds that Moscow University did not take students from Siberia[9].

In the spring of 1850 Maria and her two children left Moscow for St. Petersburg. The University in Petersburg would not take Dmitrii, who

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[6]The Decembrists were a group of noble young army officers who had made an unsuccessful attempt in December 1825 to overthrow the Tsarist regime in favour of a parliamentary system. Those who were not shot were exiled to Siberia. (See, for example, Seton-Watson, Bibl.106, pp.183-198, 750). Mendeleev much later recalled the Decembrist families of Tobol'sk in reminiscences stimulated by a visit he made to Tobol'sk in 1899 (see Colls., 12, 571).

[7]Another exiled Decembrist, N.V. Basargin, who did not live in Tobol'sk, married Dmitrii Ivanovich's eldest sister Ol'ga in 1847.

[8]Bibl.83, pp. 12-13. Mendeleev's widow, referred to here, was his second wife Anna Ivanovna. His first wife, Feozva Nikitichna, died in 1905, just over a year before Mendeleev himself.

[9]Regulations at the time were such that Siberians were restricted to Kazan' University.

had then thought of joining the Medico-Surgical Academy, but gave up this idea after fainting while attending an autopsy as an observer. After much difficulty with bureaucracy Dmitrii eventually gained entry to the Main Pedagogical Institute (where his father had trained).

Mendeleev began his course at the Main Pedagogical Institute in the autumn of 1850, as a student in the physico-mathematical faculty[10]. Very shortly afterwards, on 21st September (O.S.) 1850, his mother died (in Petersburg). Many years later, in 1887, Mendeleev dedicated one of his books[11] to the memory of his mother, with the following words:

> In memory of a mother,
> Maria Dmitrievna Mendeleeva.
>
> This investigation is dedicated to the memory of a mother by her last-born child. She was able to raise him only by her toil, by conducting the business of a factory. She instructed by example, corrected with love, and in order to devote him to science she took him out of Siberia, thus expending her last resources and strength. Dying, she left this testament: refrain from Latin self-delusion[12], insist upon work and not words, and patiently seek divine or scientific truth[13]; for she understood how often dialectics deceive[14], how much there is still to be learned, and how, with the help of science, without coercion, lovingly but firmly, prejudices, falsehood and errors are eliminated, and we achieve the safe-guarding of acquired truth, freedom for further development, the common good, and inner well-being. A mother's dying words are held sacred by D. Mendeleev[15].

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[10] There were two faculties in the Institute, the other being the historico-philological faculty.

[11] The investigation of aqueous solutions according to their specific gravity (R.), St. Petersburg, 1887. (Reprinted in Colls.,3; and in Bibl.73).

[12] Mendeleev had a lifelong distaste for Latin, and for the sterile sophistical attitudes which he saw as "Latinity" (Latinstvo) or "Latin self-delusion" (latynskoe samoobol'shchenie), and with which he seems to have associated "dialectics" (see n.3). The origin of his dislike of "Latinity" was attributed by Mendeleev to the influence not only of his mother, but also of his childhood nanny (niania) (see Colls.,23, 96; and Almgren, Bibl.5, pp.53-4).

[13] "Divine" (bozheskaia) and "scientific" are used by Mendeleev as synonyms in qualifying "truth" (pravda), not as denoting different aspects of truth: "divine" as used by Mendeleev in this sense means something akin to "absolute", without any religious connotation. Elsewhere Mendeleev contrasts "subjective-human truth" (sub"ektivno-liudskaia pravda) with "objective-divine truth" (ob"ektivno-bozheskaia pravda), the former being merely "appearance", the latter "empirically confirmed fact" (see K poznaniiu Rossii, 2nd edn., St. Petersburg, 1906, pp.50-51, n.16; and also a remark of 1887 given in Bibl.73, p.402, n.1).

[14] Mendeleev appears to be using the term "dialectics" here (as elsewhere) not in any Hegelian or neo-Hegelian sense, but rather in the classical sense of "enquiry by discussion", the practice of dialectics in this sense being unfavourably compared by him with the scientific method of investigation by observation and experiment.

[15] Bibl.73, p.379.

The Main Pedagogical Institute in Petersburg used the same buildings as the University[16]. Most of its teaching staff were also professors at the University or members of the Academy of Sciences, some being both. The student body numbered about a hundred. As a student in the physico-mathematical faculty Mendeleev was taught by the following distinguished figures:

Emil Lenz (physics; academician, and professor at the University),
M.V. Ostrogradskii (mathematics; academician),
A.N. Savich (astronomy; professor at the University),
A.A. Voskresenskii (chemistry; professor at the University),
S.S. Kutorga (mineralogy; professor at the University),
F.F. Brandt (zoology; academician),
I.O. Shikhovskii (botany; professor at the University),
F.I. Ruprecht (botany; academician),
and N.A. Vyshnegradskii (pedagogics; professor at the Institute).[17]

Lenz was the discoverer of what has come to be known as "Lenz's Law" (direction of induced current). Vyshnegradskii was later prominent in obtaining public education for women in Russia, a cause which Mendeleev also was to support.

Mendeleev's earliest publications, which appeared while he was still a student at the Institute, show primarily the influence of Kutorga's course, being concerned mainly with topics of a mineralogical nature[18]. Prominent among Mendeleev's mineralogical interests at this time was the phenomenon of isomorphism[19], his study of which played a significant part in leading him later to the discovery of the periodic law[20].

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[16]The Main Pedagogical Institute was abolished in 1858.

[17]For an account in English of the work of these scientists, see Vucinich, Bibl.125, passim.

[18]Mendeleev's first publication was Chemische Analyse des Orthits aus Finnland (transl. into German by Kutorga from Mendeleev's Russian manuscript), Verhandlungen der K. Russ. mineralog. Ges. zu St. Pet., 1854, 234-9. A Russian version is given in Colls., 15, 17-19.

[19]Mendeleev's final (Kandidat's) dissertation for his course at the Main Pedagogical Institute was on isomorphism: see Colls., 1, 7-137.

[20]See Dobrotin, Bibl.16: The early period of D.I. Mendeleev's scientific activity as a stage on the path towards the discovery of the periodic law, (R.).

But probably the most influential upon Mendeleev of his teachers at the Institute was Voskresenskii[21]. Voskresenskii, who later in the 19th century came to be known as "the grandfather of Russian chemistry"[22], had studied chemistry under Mitscherlich, Rose and Magnus in Berlin, and under Liebig in Giessen. Liebig is reported by Mendeleev to have once said (in 1860, in Munich) that he considered Voskresenskii to have been the most talented of all of his students[23]. Mendeleev's recollection of Voskresenskii as a teacher refers to the latter's insistence upon the importance of experimental work, and also his fairness in presenting the views of opposing schools in connection with theoretical questions:

> ... in the laboratory with Voskresenskii we frequently heard his favourite saying: "it is not the gods who fire pots and make bricks" ("ne bogi gorshki obzhigaiut i kirpichi delaiut"), and therefore in the laboratories which were run by Voskresenskii we were not afraid to put our hands to the affairs of science, attempting to fashion and fire the bricks out of which is built the edifice of chemical knowledge. ... Voskresenskii always clearly saw that true knowledge cannot be confined to a one-sided view, and he therefore made us beginners contrast the ideas and views of Berzelius and Liebig with the teachings of Dumas, Laurent and Gerhardt which were at that time already gaining prominence but which were still far from dominant. ... Voskresenskii already clearly saw the superiority of the ideas of the French school...[24].

From the very beginning of his undergraduate days at the Main Pedagogical Institute Mendeleev had suffered from tuberculosis, which forced him to spend much time in the infirmary of the Institute. Despite the great problems which this presented, he nevertheless managed to complete the course in 1855, receiving a gold medal for excellence. He was retained by the Institute in order to prepare for the Master's degree. Because of his ill health Mendeleev was unable to remain in Petersburg, and was assigned to the post of senior teacher in natural sciences at the gymnasium in Simferopol', in the Crimea. He was considered at this time, by the well-known Petersburg physician Zdekauer, to have only

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[21] A biographical article on Voskresenskii has been written by Figurovskii and Elagina, Bibl.22. An obituary by Mendeleev (1880) is given in Colls., 15, 335; and a slightly longer biographical sketch by Mendeleev (1892) in Colls., 15, 622-5.

[22] This epithet was occasionally applied also to N.N. Zinin (1812-1880).

[23] See Colls., 15, 622-3.

[24] 1892: Mendeleev in Brockhaus-Efron, Bibl.11, vol. 6, p.243. Given in Colls., 15, 624.

8 or 9 months to live.

Mendeleev arrived in Simferopol' in the late summer of 1855, but because of the Crimean War was soon transferred to the gymnasium at Odessa. At about this time he consulted the eminent Russian physician N.I. Pirogov, who after examining and treating him told Mendeleev, "You will outlive us both [sc. both Pirogov and Zdekauer]"[25], a prediction which was indeed fulfilled. Throughout his life, however, Mendeleev was prone to illness[26], and during the 1890's he had a serious recurrence of tuberculosis.

While teaching in Odessa, Mendeleev at the same time prepared for his Master's examination and wrote his Master's dissertation Udel'nye ob"emy (Specific volumes)[27]. By the spring of 1856 his health had improved greatly, and in May he returned to Petersburg. In this month he sat his Master's examination, and in September defended his dissertation, obtaining as a result the degree of Master of Chemistry.

In January 1857 Mendeleev was appointed privat-docent in the chemistry department of St. Petersburg University, and was also nominated secretary of the physico-mathematical faculty[28]. During the spring semester of the academic year 1856-7 he read lectures on theoretical and historical chemistry; in 1857-8 and during the first semester of 1858-9 he read lectures on organic chemistry and supervised practical work[29]. In his lectures on organic chemistry Mendeleev used the new "unitary" ideas of Laurent and Gerhardt.

In the spring of 1859 Mendeleev was sent abroad on a two-year study-trip "for advancement (usovershenstvovaniia) in the sciences"[30], which he spent mainly in Heidelberg. At first he worked in Bunsen's laboratory, but soon set up a small laboratory of his own in his private quarters. Here

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[25] See Figurovskii, Bibl. 23, p.34.

[26] For example, illness prevented him from presenting in person to the Russian Chemical Society his first paper on the periodic law in 1869.

[27] Given in Colls., 1, 139-311.

[28] The chemistry department was a department of the physico-mathematical faculty.

[29] These and subsequent connections of Mendeleev with St. Petersburg University are outlined in Makarenia and Filimonova, Bibl. 61.

[30] See Mladentsev and Tishchenko, Bibl.82, p.157.

he investigated the capillarity and thermal expansion of liquids, and in 1860 discovered the existence of what he called the "absolute temperature of boiling", later called "critical temperature" by Andrews[31]. At Heidelberg Mendeleev was a member of a social circle of young Russians which included also A.P. Borodin, a chemist who was later to become a famous musical composer as well as Professor of Chemistry at the St. Petersburg Medico-Surgical Academy[32]. Both Mendeleev and Borodin attended the Karlsruhe Congress in September 1860, at which Cannizzaro drew a clear distinction between the concepts of "atom" and "molecule" on the basis of Avogadro's hypothesis[33].

In February 1861 Mendeleev returned to Petersburg. Shortly afterwards he began writing a textbook on organic chemistry which he completed by June 1861[34], and for which in the following year he received the Demidov prize of the St. Petersburg Academy of Sciences[35]: many years later (1899) he wrote, "... this book established my name in Russia, because it circulated rapidly and widely."[36] In the autumn of 1861 Mendeleev again began to give lectures on organic chemistry in the University.

In 1862 Mendeleev married Feozva Nikitichna Leshcheva. Their first child, Masha, died soon after birth in 1863. In 1865 a son, Vladimir, was born, and in 1868 a daughter, Ol'ga[37]. The marriage was not a happy one, and did not last[38].

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[31] Mendeleev's discovery of critical temperature, ten years before its re-discovery by Andrews, was first reported in his article Sur la cohésion moléculaire de quelques liquides organiques, Comptes rendus, 50 (1860) 52; a subsequent account was given by him in Über die Ausdehnung der Flüssigkeiten beim Erwärmen über ihren Siedepunkt ("Absoluter Siedepunkt"), Annalen (Liebig), 119 (1861) 1-11. Russian translations of these papers are included in Colls., 5.

[32] An account of the life of Borodin is given in N.A. Figurovskii and Iu.I. Solov'ev, Aleksandr Porfir'evich Borodin (R.), Moscow-Leningrad, 1950.

[33] Other Russians who attended the Karlsruhe Congress were Zinin, Shishkov, Natanson, Savich and Lesinskii. On the subject of the Karlsruhe Congress and its significance for chemistry, see later, Chs.III (section A) and VIII.

[34] Organicheskaia Khimiia, St. Pet., 1861. A second edition was published in 1863; this has been reprinted in Colls., 8, 35-602.

[35] Value 1,000 roubles.

[36] See Colls., 25, 696.

[37] Vladimir died in 1898. Ol'ga long outlived her father; in 1947 she published a book entitled Mendeleev and his family (R.), Bibl. 122.

[38] See below.

During the 1860's Mendeleev was much involved in technological considerations. Between 1862 and 1867 he produced the Tekhnicheskaia entsiklopediia po Vagneru, a translated, edited and enlarged version of J.R. Wagner's Theorie und Lehrbuch der Technologie. In 1863 he went to Baku as an adviser in connection with the development of the oil-fields. The interest in oil and the oil industry which this visit aroused in Mendeleev remained with him throughout his life[39]: he visited Baku a number of times later, he visited the oil-fields of Pennsylvania in 1876, and from the theoretical side he made the suggestion (1877) that oil originates from the action of water upon metallic carbides in the interior of the earth[40].

In January 1864 Mendeleev was elected professor in the St. Petersburg Technological Institute, a post which he held until 1872. Also in January 1864 he was promoted to the status of docent in the University. In November of the same year he submitted to the University a thesis entitled Rassuzhdeniia o soedinenii spirta s vodoi (Considerations on the combination of alcohol with water)[41] for the degree of Doctor of Chemistry, successfully defending this thesis in February 1865. He was then (27th Feb., O.S.) elected extraordinary professor of physical chemistry in the Department of Technology of the University; and in December of the same year he was elected ordinary professor of technical chemistry in the Department of Technology. In the autumn of 1867 Mendeleev became professor of general chemistry at the University. At that time he was the only professor in the chemistry department of the physico-mathematical faculty. With the election of A.M. Butlerov to the department in 1868 as professor of organic chemistry[42], Mendeleev became professor of inorganic chemistry[43].

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[39] For an account of "Mendeleev and Petroleum (1863-1881)" see Almgren, Bibl. 5.

[40] Mendeleev's hypothesis about the origin of oil was presented in J. Russ. Physico-Chem. Soc., 9 (1877) 36-7: given in Colls., 10, 14-15.

[41] Given in Colls., 4, 1-152; and Bibl. 73, pp.9-214.

[42] Butlerov was the Russian pioneer of structural organic chemistry.

[43] By 1869 a third section had been established in the chemistry department at Petersburg University, that of analytical and technical chemistry. The head of this section was N.A. Menshutkin, who in 1876 came to be elected professor of analytical chemistry at the University.

Mendeleev retained his chair at Petersburg University until 1890, when he resigned.[44]

Between 1868 and 1871 Mendeleev was preparing his textbook on general and inorganic chemistry, Osnovy Khimii (Principles of Chemistry); the first part was published in 1869, and a second part in 1871[45]. In the course of writing this book Mendeleev discovered the periodic law of the chemical elements, drawing up his first periodic table on 17th February (O.S.; 1st March, N.S.) 1869. His first article on periodicity was read to the newly-formed Russian Chemical Society[46] on 6th March (O.S.) 1869 by N.A. Menshutkin, Mendeleev himself being absent through illness.

In 1871 Mendeleev published his now famous predictions of the existence and detailed properties of three unknown elements which he called "eka-aluminium", "eka-boron" and "eka-silicon", later shown to correspond to the elements gallium, scandium and germanium respectively[47].

During the 1870's Mendeleev spent much time in research on the elasticity of gases. His work on rarefied gases, which he linked with the question of the nature of the luminiferous ether, led him in the mid-1870's to an interest in the upper layers of the atmosphere, and thence to an interest in meteorology and aerostats. Later, in 1887, Mendeleev actually made a balloon trip, to observe the sun during the course of a total eclipse.

In 1875-76 Mendeleev gave three public lectures in which he criticised the ideas and claims of the spiritualists[48]. Spiritualism was rather

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[44] The circumstances of Mendeleev's resignation are outlined briefly below.

[45] Seven further Russian editions of this work were published during Mendeleev's lifetime (Bibl.65), as well as three English editions (Bibl.66), one German edition (Grundlagen der Chemie, St. Petersburg, 1891; Leipzig, 1892: from R-5, 1889) and one French edition (Principes de chimie, Paris, 1895-99: from R-5, 1889). Five posthumous Russian editions have been published - in 1927-28, 1931, 1932, 1934 and 1947; the first volume of the two-volume 1932 edition has been published in Armenian translation, 1935; and the 1947 edition has been published in Rumanian translation, 1957-58.

[46] The Russian Chemical Society had been founded in the autumn of 1868, Mendeleev being an active founder-member.

[47] "Eka" is the Sanskrit for "one". These predictions, and others made by Mendeleev, are considered in detail in Ch.VI.

[48] See Colls., 24, 171-240.

fashionable in Petersburg at the time, among its adherents being Butlerov, Mendeleev's chemical colleague at the University.

In 1882 Mendeleev married for a second time. His new wife was Anna Ivanovna Popova, whom he had met in 1876 when she was a 17-year old art student. Mendeleev was now officially a bigamist, but a blind eye was turned to this[49]. This second marriage, unlike the first, was very happy. Four children were born - Liubov' (1881, O.S.; 1882, N.S.), Ivan (1883) and the twins Maria and Vasilii (1886, O.S.; 1887, N.S.)[50]. Anna introduced Mendeleev to the world of art, his interest in the subject becoming such that in 1893 he was elected to the St. Petersburg Academy of Arts.[51]

In significant contrast to Mendeleev's election later in his life to the Academy of Arts was the fact that he was never elected to full membership of the St. Petersburg Academy of Sciences. He had been made an associate member (or "corresponding member"; chlen-korrespondent) in 1876; but as a candidate for full membership (to become an "actual member", deistvitel'nyĭ chlen) in a ballot of 1880 he was blackballed. The explanation of this seemingly strange state of affairs lies in the animosity which Mendeleev has aroused against himself in certain high-ranking officials of the Education Ministry and Academy of Sciences, by his open criticism of an increasing tendency shown by these officials to attempt to curtail scientific expansion in the University in favour of the traditional classical curriculum[52]. Notable in this respect were the

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[49]The tolerance of Mendeleev's bigamy by the authorities shows the esteem in which he was now held, this being illustrated further by the following story related by Ozarovskaia in her recollections of Mendeleev (Bibl.88, pp.135-40). Shortly after Mendeleev's second marriage a nobleman in a similar situation appealed to the Tsar for permission to remarry, citing the case of Mendeleev as precedent. The Tsar refused, saying, "Mendeleev has two wives, yes, but I have only one Mendeleev."

[50]Liubov' was born about 4 months before Mendeleev married Anna Ivanova, but her birth was not registered until after the wedding (see Colls., 25, 676). Liubov' was later to marry A.A. Blok, the famous Russian poet. Maria became Director of the D.I. Mendeleev Museum-Archive at Leningrad University; her work in the Museum-Archive included the preparation for publication of the material given in Bibl.70 (1951).

[51]Recollections of "Mendeleev in life" (R) by Anna Ivanovna were published in 1928 (Bibl.76).

[52]This education policy, which came to be adopted in the 1870's, was directed against what were seen as the politically dangerous "liberalising" effects of science education in the University; it was undoubtedly seen by some also as a means of ensuring the continued dominance of the Academy of Sciences in the field of science.

hostile relations between Mendeleev and Count D.A. Tolstoi, who was Minister of Public Education during the 1870's and early 1880's, and who became President of the Academy of Sciences in 1882[53].

In the 1880's Mendeleev resumed the experimental investigation of aqueous solutions which he had begun in the early 1860's in connection with his research for his doctorate. He developed what was called the "hydrate theory" of aqueous solution, publishing his results in 1887 in the large monograph entitled Issledovanie vodnykh rastvorov po udel'nomu vesu (The investigation of aqueous solutions according to their specific gravity)[54].

From the 1880's onwards Mendeleev received an assortment of medals, honorary degrees and honorary memberships of learned societies in recognition of his work, particularly for the discovery of the periodic law. In England, for example, he was awarded the Davy Medal (jointly with Lothar Meyer) by the Royal Society in 1882; in 1883 he was elected an honorary foreign member of the Chemical Society, in 1889 receiving the Faraday Medal of the Society; in 1892 he was elected a foreign member of the Royal Society, and in 1905 was awarded the Copley Medal of the Society[55]. He received similar honours in many other countries.

In 1890 Mendeleev resigned his chair at Petersburg University. This was prompted by the rebuff which he had received on attempting to present a petition to the Minister of Education (Count Delianov) from the students, requesting the relaxation of certain academic rules. But Mendeleev's resignation was not a reaction solely to this incident: it represented the culmination of his increasing frustration and disagreement with the Ministry of Education. Mendeleev did not withdraw his resignation, despite requests from the University that he do so.

In May 1890 Mendeleev was recruited by the Naval Ministry to help in the organisation of the Russian gunpowder industry. In 1891 he was elected Consultant to the Naval Ministry in connection with the affairs of their

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[53] A brief account in English of Mendeleev's relations with the St. Petersburg Academy of Sciences is given in Leicester, Bibl.56.

[54] See above, n.11. An account of Mendeleev's theory of solution is given in Storonkin and Dobrotin, Bibl. 111.

[55] A brief chronological survey of Mendeleev's scientific contacts with Britain by the present author is shortly to be published by Leningrad University as Khronologicheskii ocherk sviazei D.I. Mendeleeva s uchenymi Velikobritanii, in Istoriia i metodologiia khimii, vyp. 1, 1975.

Scientific and Technical Laboratory. In November 1892 he became Scientific Custodian of the St. Petersburg Depot of Standard Weights and Measures; and just over six months later was appointed Director of the Central Chamber of Weights and Measures, newly formed from a reorganisation of the old Depot[56]. He retained this post for the rest of his life, contributing greatly to the field of metrology during this period.

Around the turn of the century Mendeleev wrote much in connection with industrial, economic and politico-sociological topics. Among his scientific writings of the early 20th century was an article on his "chemical conception" of the luminiferous world-ether as the lightest chemical element[57].

In an undelivered letter (addressed to Count Witte) dated August (O.S.) 1903 Mendeleev reviewed his services "to motherland and to science", listing three fields of contribution: his scientific work, his teaching activities, and his "third service" to Russian industry[58]. Two years later in a diary entry Mendeleev wrote that in the field of science "four subjects above all have made my name: the periodic law, research on the elasticity of gases, the understanding of solutions as being associations, and the 'Principles of Chemistry'. ... These 'Principles of Chemistry' are my favourite child. In them is my image, my attempt at pedagogy, and my sincere scientific ideas."[59]

In the autumn of 1906 Mendeleev drew up a manuscript chronology of the main events in his life - Biograficheskie zametki.[60] About three months after completing this survey, on 20th January (O.S.; 2nd Feb., N.S.) 1907, he died of pneumonia.

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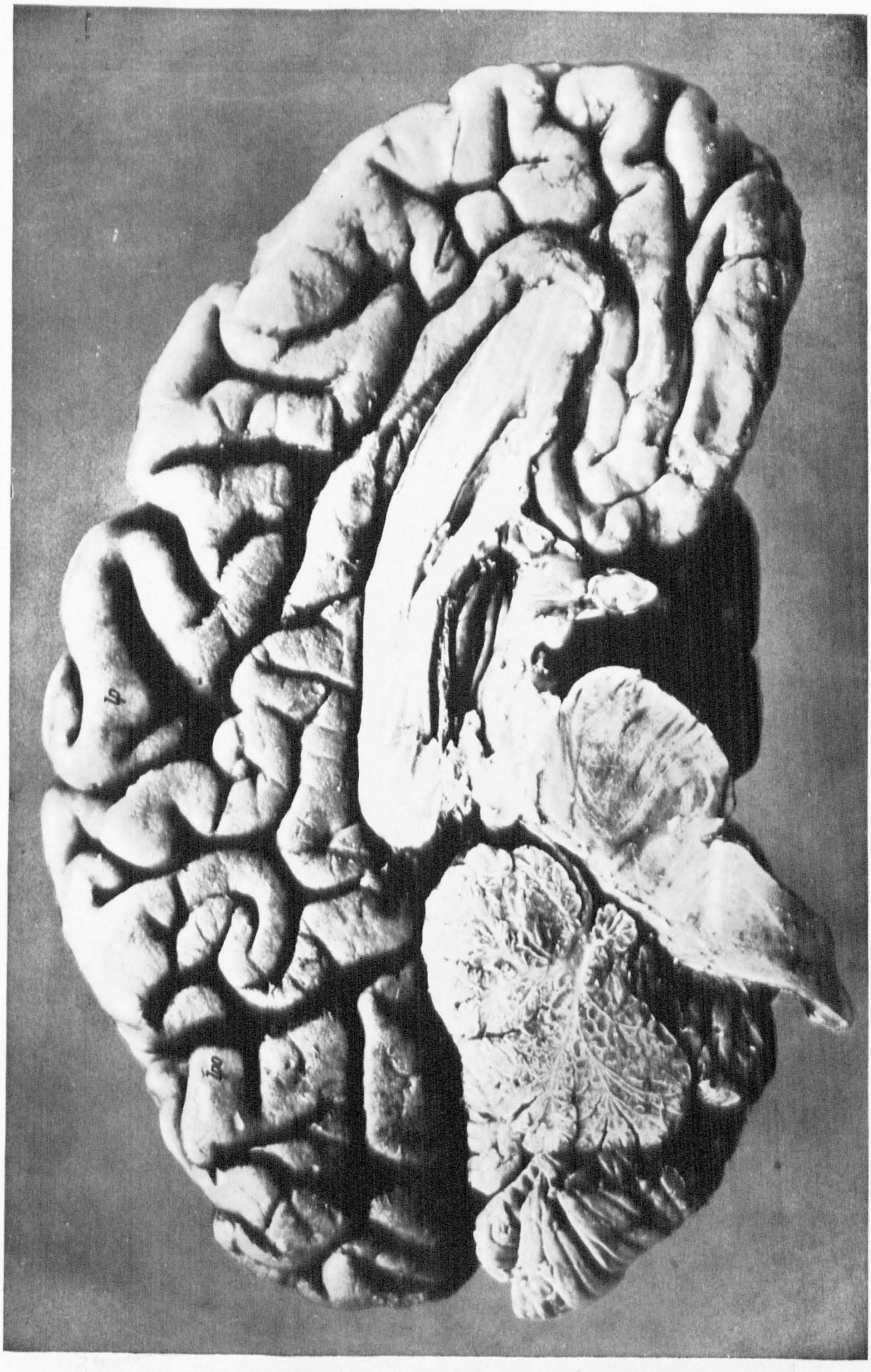
[56] Mendeleev obtained this post through the influence of Count S. Witte, Minister of Finance 1892-1903.

[57] Mendeleev's "chemical conception" of the ether is discussed later, in Ch. I (section C) and Ch. VI (Section C).

[58] This letter is published in Bibl. 70, pp. 31-33. The reference here by Mendeleev to his "third service" is the source of the title of Almgren's thesis, Bibl. 5.

[59] Published in Bibl. 70, pp.34-35.

[60] Published in Bibl. 70, pp.13-30; and in Colls., 25 667-685.



Photograph of Mendeleev's brain.
(Bechterew and Weinberg, 1909:Bibl.6).

CHAPTER I

PERSISTING ENTITIES IN MENDELEEV'S CONCEPTION OF THE MATERIAL WORLD

A. Introduction

All Mendeleev's scientific hypotheses about the structure of the world were attempts at explanation in terms of two fundamental eternal (or "persisting") categories, "matter" and "motion"[1]. Although in his later writings (from about the mid-1880's) Mendeleev recognised also a third fundamental category, "spirit"[2], when discussing his ontological beliefs[3], he never elaborated upon the nature or significance of this category[4]; and unlike the categories of matter and motion this third aspect of Mendeleev's

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[1] "Matter" (materiia) was sometimes expressed by Mendeleev as "substance" (veshchestvo). The category "motion" (dvizhenie) was sometimes referred to as "energy" (energiia), all forms of energy being seen as forms of motion; sometimes this category was viewed alternatively as "force" (sila). An account of "The problem of matter and motion for Mendeleev" (R.) is given by Kedrov in Bibl.35, pp.215-222.

[2] Russian dukh; sometimes expressed by Mendeleev as "psyche" (psikhoz).

[3] The term "ontology" is used in the present discussion not in its more traditional meaning of "the doctrine of being as such", but in the sense of "the doctrine of the fundamental eternal categories of nature"; this latter sense closely resembles that proposed by Bunge, who describes ontology as "the discipline dealing with basic categories such as object, space, time, and change" (Mario Bunge: Scientific Research I, The Search for System, Studies in the Foundations, Methodology and Philosophy of Science, vol.3/1, Springer-Verlag, Berlin-Heidelberg, 1967; p.25).

[4] The trinitarian ontology - in terms of matter (substance), force (or energy, motion) and spirit (psyche) - which lies at the base of Mendeleev's empiricist world-view of so-called "realism" is discussed by him particularly in the following sources:

i) Attempt at a chemical conception of the world-ether (R.), in Vestnik i biblioteka samoobrazovaniia, 1903, No. 1, 2, 3, 4; reprinted 1905 (reproduced in PLBA, 470-517);

ii) Zavetnye mysli (Hidden ideas), 1903-5, St. Petersburg (see Colls.24); and

iii) Mirovozzrenie (World-view), manuscript dated 27 Sept., 1905; unpublished until 1948, when it was included in Nauchnoe naslodstvo, vol.I, Moscow, pp. 157-62 (see also Colls., 24).

later ontology played no part in moulding the form of his scientific theorising[5].

Mendeleev's belief in matter as a fundamental eternal category was founded upon the empirical law of conservation of weight. The law of conservation of energy (alternatively expressed by Mendeleev as "the law of the indestructibility of forces"[6]), coupled with the generalisation that all forms of energy represent some kind of motion of matter[7], led to his recognition of the fundamental category which could be expressed either as "force", or, from a different standpoint, as "energy" - or, more precisely, as 'motion". In a diary entry dating from September 1871 Mendeleev outlined a plan for a proposed public lecture: he included in this plan the note, "The conservation of weight and of motion as the fundamental laws of science."[8] Shortly afterwards he commented in the same diary upon the ontological significance of "the law of conservation of motion": "We seek something eternal in the midst of the transient - at present such an eternal thing is motion. That which is eternal has been idolised, has formed the heart of philosophical doctrines. And we are not strangers to this. Nowadays motion is eternal."[9]

The essential restrictions imposed upon the character of Mendeleev's scientific theories by this matter-plus-motion framework were -

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[5]For example, even in his Attempt at a chemical conception of the world-ether (R.), which contains an explicit presentation of his trinitarian ontology, Mendeleev hypothesizes about the ether solely within a matter-plus-motion framework (see later). However, he seems to have been concerned with the question of the role of the category "spirit" in science when he wrote in 1902, "... must we acknowledge that there is spirit in matter and forces? Radioactive substances, spiritualism?" (notebook extract, MALU); and it is perhaps the fact that the atomic theory ignores the category "spirit" which prompted him to write in Pr.Ch., R-7 (1902-3), "I have no doubt that the atomic theory ... has its philosophical defects proper to materialism" (op.cit., 157, n.30 bis; see also Pr.Ch.,E-3, I, 216, n.30a).

[6]Or "the law of the eternity of forces" - referring not to particular forces, but to the conservation of forces in general by means of the conversion of particular forces into other equivalent forces. The use of such a term as an alternative to "the law of conservation of energy" is found, for example, in the introduction to Pr.Ch., R-7 (given in English translation in Pr.Ch., E-3).

[7]This is a generalisation from the kinetic theory of heat, e.g., in Pr.Ch., R-1, Mendeleev says, "... at the present time we cannot but represent a particular thermal state of matter as a definite state of motion of the particles of matter. We may think that all phenomena observed by us are various forms of motion" (Colls., 13, 486-7).

[8]Sc.Ar., 622.

[9]Ibid., 623.

i) the assumption of necessary concomitance of matter and motion, i.e., the denial of absolute rest in nature;

ii) the infusibility of the categories of matter and motion into a single ultimate fundamental category;

iii) the eternity (persistence) of matter, i.e., the conservation of the quantity of matter;

and

iv) the eternity (persistence) of motion, in the sense of the conservation of energy (all forms of which were taken to represent some kind of motion of matter).[10]

Because Mendeleev did not draw a sharp line of demarcation between the ontological categories as regards their relationship to macroscopic matter, the above restrictions allow much more scope in the construction of scientific theories than might at first seem to be the case. Certainly, the ontological category of matter was arrived at by Mendeleev by generalisation from what is called "matter" in the macroscopic or "sensible"[11] world; and the assumption of its persistence was founded upon the empirical law of conservation of weight, weight being traditionally taken as a measure of the quantity of macroscopic matter. But the lack of strict demarcation between Mendeleev's ontological categories of matter and motion as regards their relationship to macroscopic matter permits weight to be thought of not as a property solely of the fundamental category matter, but as a compound effect of matter and some kind of concomitant "inner motion". This enables the concept of "weight" (and of "mass" in the purely pondero-inertial sense, as distinct from the sense of "quantity of matter") to be partially divorced from the concept of "quantity of matter"; and by invoking the idea of the convertibility of part of the "motion-component" of weight into some other form of motion which does not contribute to weight, or vice-versa, the possibility arises of constructing a theory which allows non-conservation of weight but which is still strictly bound by the restriction of conservation of the quantity of matter[12]. In fact such a possibility was actually acknowledged by Mendeleev himself, for

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[10] These four demands are clearly expressed in the sources listed in n.4, above.

[11] "Sensible" is here used to mean "perceptible to the senses".

[12] Because of this possibility, refutation of the law of conservation of weight would not necessarily refute Mendeleev's ontology - only a total loss of weight for a closed system in a constant gravitational field would refute it.

example in a discussion of Prout's hypothesis in 1871 where he suggests that a transmutation of chemical elements may be accompanied by a breakdown in the law of conservation of weight:

> Even if we agree that the matter of the elements be all of the same kind there are no grounds for thinking that n parts by weight of one element, or n of its atoms, will yield the same n parts by weight in a transformation into one atom of another body, i.e., that the atom of the second element will be n times heavier than the atom of the first. I consider the law of conservation of weight to be a particular case of the law of conservation of forces or of motions. Weight surely depends upon a particular kind of motion of matter, and there are no grounds for denying the possibility of the conversion of this motion into chemical energy, or some other form of energy, when the atoms of the elements are formed. Two phenomena which are now observed - the constancy of weight and the undecomposability of the elements - have at the present time a close, even historical, connection; but if a known element were to be decomposed, or a new element formed, we cannot deny that weight may be created or diminished[13].

In 1889 Mendeleev again mentions that weight may not express quantity of matter, this time presenting the idea in the form of a "fantasy" (fantaziia) of one of his students:

> ... I do not think it useless to mention a fantasy of one of my students... The atoms, according to this new utopian, may be essentially of the same kind, or different - we do not know which; we know them only in motion, and just as the motion of the heavenly bodies is conserved, so also this motion is conserved and stable. The weights of the atoms differ only in consequence of the modes and quantity of the motion which characterises them. The heaviest atoms may be simpler than the light ones - an atom of mercury may be simpler than an atom of hydrogen, only the manner in which it moves making it heavier[14].

In the 7th (1902-3) and 8th (1906) editions of Principles of Chemistry (R.) Mendeleev refers to "the conditional silent general assumption which takes weight or mass to be proportional to the quantity of substance".[15]

We see that although Mendeleev was prepared to acknowledge the possibility of a future breakdown of the law of conservation of weight (mass), he did so without rejecting his ontological commitment to the idea of the conservation of the quantity of matter; instead, he suggested the possibility of non-proportionality between weight (mass) and the quantity

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[13] Annalen (Liebig), Supplementband VIII (1871), no.2, pp.206-7 (G.) A Russian version is given in Sc.Ar., 448, and in PLBA, 157-8.

[14] Faraday Lecture: PLBA, 224.

[15] Pr.Ch., R-7, 469, n.16 bis; R-8, 619, n.413 (PLBA, 326). See also E-3, II, 33, n.16a.

of matter[16]. However, the empirical fact remained that the law of conservation of weight (mass) had not been contravened; and this resulted in Mendeleev's pragmatic acceptance, in nearly all his scientific work, of weight (mass) as being a measure of the quantity of matter[17]. This latter was paralleled by a similarly pragmatic approach by Mendeleev in connection with the question of the qualitative nature of matter. Although he acknowledged that the complexity of the chemical elements is quite possible - even likely - he recommended nevertheless that until there is empirical proof of their transmutation we should treat the elements as qualitatively-

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[16]Mendeleev, in such passages as those quoted above, can be considered as having anticipated the phenomenon of "mass defect" (or of "packing fraction") in the atomic nucleus, as has already been pointed out elsewhere, e.g., by H.R. Paneth, 1952 (Bibl.91, p.68), Makarenia, 1965 (Bibl.60, 17) and Sambursky, 1969 (Bibl.101, p.104). But to go beyond this and claim anticipation by Mendeleev of the explanation of mass defect by mass-energy interconvertibility or equivalence - as Paneth (loc.cit.) and Sambursky (loc.cit.) have done - requires careful qualification. The original theory of mass-energy interconvertibility proposed by Einstein recognised a contribution to the mass of a particle from the kinetic energy of the particle; also, for the case of a composite particle it recognised not only a contribution to the rest-mass of the particle from the potential energy of binding of its constituents, but also the possibility of a contribution from the kinetic energy of its constituents, i.e., from the "inner motion" of the composite particle. This early theory of Einstein's did not incorporate the idea of the interconvertibility of matter and energy; instead, the quantity of matter - defined in terms of the rest-mass of non-composite particles - was assumed to be strictly conserved. Subsequent developments of relativity theory on the other hand, by Dirac and others from the 1920's onwards, recognised a mass-energy equivalence in the sense of the interconvertibility of matter and energy. Insofar as both Mendeleev and Einstein (in his original theory) allowed the possibility of a contribution to the mass of a composite particle from the "inner motion" of the particle, within a theoretical framework which adhered strictly to the conservation of matter and energy separately, Mendeleev may be seen as foreshadowing Einstein's original theory of mass-energy interconvertibility. At the same time, however, Mendeleev's views differed from those of Einstein in two important respects: first, for Einstein all motion contributed to mass, whereas Mendeleev saw the possibility of a contribution to mass only from a certain particular type of ("inner") motion; and secondly, Mendeleev made no suggestion corresponding to Einstein's idea of a contribution to the rest-mass of a composite particle from the potential energy of binding of its constituents. As regards a comparison of Mendeleev's ideas with those of modern (post-Dirac) relativity theory, there seems to be little justification for claiming that Mendeleev anticipated the explanation of mass defect which is given by this latter theory, because the idea of mass-energy equivalence in modern relativity theory is quite alien to Mendeleev's fundamental tenet of the separate conservation of matter and of energy.

[17]Apart from the significance of its being pragmatically treated as a measure of the quantity of matter, the property of weight (mass) possessed great significance for Mendeleev also because of the number of physical

distinct ultimate forms of matter[18].

Mendeleev explicitly distinguished the following two different senses in which the term "element" is used in chemistry -

i) to denote those "concrete" or "sensible" substances which have in practice proved to be incapable of decomposition into two or more simpler substances[19], e.g. diamond, graphite, "flowers" of sulphur;

and

ii) to denote those "abstract" or "transcendental" substances which are considered to persist unchanged throughout all chemical transformations, e.g., carbon, which is considered to be contained not only in diamond and graphite, but also in carbon dioxide, benzene, etc.[20]

Mendeleev usually reserved the term "simple body" (prostoe telo)[21] for sense i) and "element" (element) for sense ii), but he was not completely consistent in this usage. Except when quoting Mendeleev we shall use the terms "simple substance" and "element" respectively.[22]

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and chemical phenomena which seemed to him to show some sort of empirical dependence upon it. For example, in various editions of Principles of Chemistry he wrote, "Gravity, attraction at small distances [sc. adhesion], and many other phenomena are found to be in direct dependence upon the mass of a substance" (PLBA, 296); and in his Attempt at a chemical conception of the world-ether (R.) he pointed to the following significance of weight (mass) in chemistry - "A true and simple understanding ... of chemical phenomena was initiated with the study of the weight (mass) of the reacting substances, the weight of molecules, and the lawfulness existing between the weights of the atoms [sc. the periodic law]. Without the conception of masses acting on one another, chemistry would be merely descriptive ... knowledge" (PLBA, 502, footnote).

[18]The lengthy topic of Mendeleev's views on "primary matter" the complexity of the elements, and also the views of his contemporaries on these questions, are dealt with in a separate chapter (Ch.II).

[19]Incapable, that is, of the decomposition reaction, A→B+C (+...).

[20]The terms "concrete" (konkretnyi) and "abstract" (otvlechennyi) are used in this context by Mendeleev himself (see, for example, PLBA, 239). The term "transcendental" is used here, following the example of F.A. Paneth (Bibl.89 and 90), in its epistemological sense of "beyond the sphere of consciousness".

[21]The Russian prostoe telo may be translated loosely also as "simple substance", although the latter would correspond more correctly to prostoe veshchestvo.

[22]Others who have discussed the distinction between "element" and "simple substance" include,

i) C.Hell, Neues Handwörterbuch der Chemie, Braunschweig,1878,vol.3,p.1;
ii) G.Urbain, Les Disciplines d'une Science, 1921, pp.75ff.;
iii) F.A. Paneth, Bibl.89, and Chemical Elements and Primordial Matter: Mendeleeff's view and the Present Position in Bibl. 90;
and
iv) J.van Spronsen, Bibl.110, pp.58-60.

Mendeleev fully appreciated that it is the elements rather than the simple substances which were systematised on the basis of the periodic law[23]; and he also recognised that the success of this periodic system of the elements provided a strong argument against the positivistic refusal to accept that elements persist in some real sense in chemical compounds.[24] It is probably no misrepresentation of Mendeleev's views to say that with the consolidation of the idea of "element" by the periodic law, chemistry for him came to be characterised simply as "the study of the elements". In fact, shortly after his discovery of the periodic law Mendeleev wrote in one of his diaries, "... everything is reduced to the elements, the entire doctrine of chemistry is the doctrine of the properties of the elements..."[25]

The fate of Mendeleev's belief in the chemical elements as the persisting invariant constituents of all simple substances and compounds was not tied to the fate of his belief in the atomic-molecular theory. The latter theory certainly provided a simple and convenient interpretation of the persistence of elements[26], and as such had become closely associated with the doctrine of the elements; but this association was not a necessary connection, as Mendeleev fully appreciated - "There is a simplicity of representation in atoms, but there is no absolute necessity to have recourse to them. The conception of ... the chemical elements is alone necessary and trustworthy."[27]

Mendeleev considered atomic weight to be a fundamental property of the elements, its significance not being restricted merely to that which it had within the atomic-molecular theory. This view, which was supported by the fact that it was the atomic weight of the elements which appeared to be the property which indicated their positions in the periodic table, is seen for example in the Principles of Chemistry, where Mendeleev says of the atomic weight, "Its magnitude indicates the relative mass of the atoms, or, if we

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[23] See below, section B.

[24] Such a view is expressed by Mendeleev particularly in an article of 1898 (PLBA, 240; see below, section B).

[25] 1871; given in Sc.Ar., 615.

[26] This is the case whether or not the elements are considered to be complex: the complexity or otherwise of the elements is reflected in the nature of the atoms.

[27] Pr. Ch., R-7 (1902-3), Ch.IV, n.33.

avoid the conception of atom, its magnitude indicates the relation between the masses which compose the chemical ... elements".[28]

Throughout his scientific career Mendeleev characterised the atomic-molecular theory as a "working hypothesis" (rabochaia gipoteza) similar in kind to the assumption in geometrical analysis that a curve is composed of infinitesimal straight lines[29]. In 1906 he expressed this sentiment as follows:

> In my opinion the atomism of our day must above all be regarded as a convenient method for the investigation of ponderable matter (a working hypothesis). As a geometer in reasoning about curves represents them as formed of a succession of straight lines, because such a method enables him to analyse the subject under investigation, so the scientific man applies the atomic theory as a means of analysing the phenomena of nature. Naturally there are people now, as in ancient times, and as there always will be, who apply reality to imagination, and therefore there are to be found atomists of extreme views; but it is not in their spirit that we should acknowledge the great services rendered to all science by the atomic doctrine... .[30]

It should be appreciated, however, that in such polemical passages as this Mendeleev does seem rather to overstate his position: as a practising chemist he does not appear to have adhered to this extreme position of regarding the atomic-molecular theory as a mere computational device.

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[28] This is from R-8 (1906) 253 (see PLBA, 287). R-7 has the same passage; in earlier editions there occur very similar, but not identical, passages, e.g., see PLSM, 348, for the corresponding passage from R-3 (1877).

[29] This geometric analogy is first found in Mendeleev's work in a summary of his lectures on theoretical chemistry, 1861 (MALU, II-A-17-9-8a, p.8). The drawing of such an analogy by Mendeleev between the atomic theory and the methods of the calculus is representative of his general tendency not to restrict his discussion of any particular topic within the commonly-recognised confines of that subject. That Mendeleev's knowledge and interests were extremely wide-ranging can readily be seen from the contents of his collected works (Bibl.68): he was probably unique in 19th-century Russia in the breadth of his interests and activities. A comparison with the 18th-century Russian polymath Lomonosov naturally springs to mind, although Mendeleev did not possess the literary talents of Lomonosov.

[30] Pr.Ch., R-8 (1906) 483; given in PLBA, 599-600.

B. Mendeleev's doctrine of the chemical elements.

The distinction between elements and simple substances was emphasised by Mendeleev from a relatively early stage in his scientific career. The earliest passage in which he points out this distinction seems to be the following, from the 1st edition of his Organic Chemistry (1861): "Because of modern nomenclature it is extremely easy to confuse body with radical ... The word chlorine is used both for the designation of chlorine gas Cl_2 and for the designation of the radical Cl".[31] Eight years later (1869), in his first article on the periodic classification of the elements, Mendeleev wrote:

> ... no matter how the properties of a simple body may change in the free state, something remains constant, and when the elements form compounds this something - a material thing - establishes the characteristics of the compounds which include the given element. In this respect we know at present only one numerical property peculiar to the element, namely the atomic weight. The magnitude of the atomic weight ... is a number which relates to ... that material part which is common to the simple body and all its compounds.[32] The atomic weight belongs not to charcoal or diamond, but to carbon.

Similarly, in 1871, in another paper by Mendeleev on the periodic law, we find the following remarks:

> The concepts and terms simple body and element are commonly confused with each other ... A simple body is a substance ... with a set of physical characteristics and chemical reactions ... By the term element we should understand those material components of the simple and compound bodies which give them their particular collection of physical and chemical properties ... Carbon is an element, but charcoal, graphite and diamond are simple bodies.[33]

These last two passages clearly show that by about 1870 Mendeleev had explicitly characterised the chemical elements as the "constant" ("unchanging", "invariant", "persistent" - postoiannye) material components of both simple substances and compounds, which produce in these simple and compound substances their collection of physical and chemical properties.

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[31] Organic Chemistry (R.), St. Petersburg, 1861, p.36, footnote. In the 2nd edition (1863) (given in Colls., 8, pp.37-602) the corresponding passage is worded slightly differently: "The word 'chlorine' is used both for the designation of chlorine gas, Cl_2, i.e., a body, and for the designation of the radical Cl" (Colls., 8, 114).

[32] J. Russ. Chem. Soc., 1 (1869) nos. 2 and 3, p.66; PLBA, 17.

[33] Annalen (Liebig), Suppl. VIII (1871), No.2, pp.133-4 (G). A Russian version is given in Sc.Ar., 344, and in PLBA, 102.

Mendeleev fully appreciated that it was the elements, rather than just the simple substances, which were systematised on the basis of the periodic law: "... the periodic law ... expresses the properties of the elements, and not of the simple bodies."[34] He was of course aware that one aspect of the periodicity of properties of the elements was the periodicity shown by certain properties of the simple substances, e.g., melting-point; but the more fundamental aspect in Mendeleev's view was the periodicity in the forms and properties of the compounds of the elements.[35]

Perhaps the clearest and most detailed expression by Mendeleev of his views on the concept of "element" in chemistry is that given by him in an article on the periodic law published in 1898, which includes the following comments:

> ... for a given element there may exist many different simple bodies... Thus, carbon ... appears in the form of charcoal, graphite and diamond, which (taken in the pure state) give, on burning, one and the same carbon dioxide gas, and in the very same quantity... The "elements" themselves ... are not liable to modification and mutual transformation, and represent, according to modern views, the unchanging essence of (chemically, physically and mechanically) changing substance, entering into both simple and compound bodies. Viewed in this way, the chemical elements turn out to be something abstract, because we neither see them nor know them. Such a realistic branch of knowledge as chemistry has arrived at this almost idealistic view on the basis of the totality of observations so far made; and if we may uphold this view, it is only as the subject of a profoundly deep-rooted conviction which has so far turned out to be in complete agreement with observation and experiment. In this sense the conception of the chemical elements has a profound and real basis in the whole science of nature, because no-one anywhere has ever transformed carbon, for example, into some other element, whereas the simple body charcoal has been transformed into graphite and diamond... The main conception with which it is possible to set about explaining the periodic law consists precisely in the fundamental distinction between the ideas of elements and simple bodies. Carbon is an element, something invariant, which is contained both in charcoal and in carbonic acid gas and illuminating gas, in diamond and in all of the changeable organic compounds, in limestone and in wood; it is not a concrete body, but a ponderable (material) substance with a particular set of properties. Just as in water vapour or in snow there does not exist the concrete body liquid water, but rather the ponderable substance with the set of properties which belong to it alone, so also

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[34] Pr.Ch., R-8 (1906) 616 (PLBA, 321). Although Mendeleev's earliest writings on the periodic law do not appear to contain such a succinct statement of this fact, they nevertheless clearly reflect his awareness of it.

[35] Mendeleev's views on the fundamental significance for the structure of the periodic system of the maximum valency shown by the elements in their "saline" oxides (or "non-peroxide" oxides) are presented later, in Chs. III and V.

all carbon compounds contain the materially-invariant carbon - not charcoal, but just carbon.[36]

J.W. van Spronsen, in his brief consideration of the distinction drawn by Mendeleev between "simple substance" and "element", misrepresents Mendeleev's position: he appears not to appreciate that for Mendeleev the elements are the constituents not only of chemical compounds, but also of the simple substances.[37] It is not difficult to fall into this error if one studies only those comments which Mendeleev makes on this subject in the introduction to the various editions of his Principles of Chemistry. For example, in the 1st edition of this work (1869) Mendeleev writes, "... it is useful to make a clear distinction between the conception of a simple body as a separate homogeneous substance, and as a material - but unobservable - part of a compound body"; and in the 8th edition (1906) the corresponding sentence reads, "... it is useful to make a clear distinction between the conception of a simple body as a separate homogeneous substance, and as a material part or element of a compound substance."[38] These remarks do not indicate that the elements (as distinct from the simple substances) were considered by Mendeleev to be the components not only of compounds but also of the simple substances. On the other hand, there is nothing here which expressly denies this latter interpretation of "element"; and a perusal of Mendeleev's many discussions of this subject in his other writings (such as, for example, the passages quoted earlier in this section) leaves no doubt as to his view that the elements are indeed components also of the simple substances. Since Spronsen cites not merely the misleading Principles of Chemistry, but also the passage (quoted earlier) from Liebig's Annalen of 1871 where Mendeleev explicitly characterises the elements as the "material components of the simple and compound bodies", his misrepresentation of Mendeleev's position on this matter is rather surprising.

Despite Mendeleev's many comments to the effect that there is a real material persistence of elements in their compounds, we also find, in his

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[36] Brockhaus-Efron, Bibl.11, vol. 23, half-vol. 45, pp.311-2 (PLBA,237-9).

[37] Spronsen, Bibl.110, pp. 58-60.

[38] Pr.Ch., R-1: Colls., 13, 73-4. Pr.Ch., R-8: Colls., 24, 72. Similar passages are to be found in the intervening six editions of Pr. Ch.

Principles of Chemistry, certain remarks which could be - and indeed have been[39] - interpreted as a concession to the positivistic point of view that the law of conservation of the chemical elements is no more than an expression of the fact that the simple substances which react to form a given compound are always recoverable, and in precisely their original quantities, from this compound:

> ... if we say ... that oxygen is contained in red mercury oxide, then by this we do not wish to say that oxygen as a gaseous substance is contained in this complex body, but we only wish to express those transformations of which red mercury oxide is capable ... In short, we may say that the composition of a compound is an expression of those transformations of which it is capable.[40]

Taken in isolation, this passage certainly seems to convey a positivistic interpretation by Mendeleev of the law of conservation of the chemical elements. On this matter F.A. Paneth has commented:

> ... the ... law of the conservation of the chemical elements ... is nowadays accepted by all chemists, even though formerly liberties were occasionally taken with its interpretation; e.g., St. Clair Deville and Ostwald put forward the view that it did not imply anything more than that chemical elements could be recovered from their compounds. Mendeleeff too makes some concession to this point of view when he says: "the composition of a compound is the expression of those transformations of which it is capable"...
>
> Mendeleeff ... seems to have believed too strictly in the overthrow of metaphysics by Lavoisier, and to have shared his allergy to the inheritance of the Greek philosophers ... This is the only probable explanation of his above-mentioned predilection for the erroneous view of Ostwald that chemical formulae indicate only possible changes... .[41]

However, the overwhelmingly non-positivistic (and even anti-positivistic) character of Mendeleev's views in general on the chemical elements contrasts so starkly with these prima facie positivistic sentiments from Principles of Chemistry that the thought arises that a positivistic interpretation of this passage, such as that given here by F.A. Paneth, is perhaps mistaken. Not only does Mendeleev talk frequently of the real material persistence of the elements, but in 1898 he even criticised explicitly the positivistic refusal to accept the idea of such persistence: in support of his argument against the view that the idea of persisting material elements is an abstraction with no foundation in, and no

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[39] Notably by F.A. Paneth, Bibl. 90.

[40] Pr.Ch., R-1 (1869): Colls., 13, 73. A corresponding passage, with only very slight, and insignificant, differences in wording, is found in each of the subsequent editions of Pr.Ch.

[41] Bibl.90, pp.64-5.

correspondence to, reality, Mendeleev cited the success of the periodic law, a success which would be difficult to comprehend without the assumption of a real persistence of the elements - "Such conceptions of extreme ... positivism ... are refuted by - among other things - the purely real consequences arising from the periodic law, which governs the imagined elements ... ."[42] Rejection of a positivistic interpretation of the above-quoted passage from Principles of Chemistry would seem to be further supported by the following two points -

i) Not only does a positivistic interpretation of the passage contrast sharply with the nature of Mendeleev's remarks elsewhere, but it is in sharp contrast also with its immediate context. Thus, following immediately after the words "the composition of a compound is an expression of those transformations of which it is capable" is the sentence, "In this respect it is useful to make a clear distinction between the conception of a simple body as a separate homogeneous substance, and as a material - but unobservable - part of a compound body."[43]

ii) The passage in question is to be found in all eight editions of Principles of Chemistry which were published during Mendeleev's lifetime. If it really were an expression of sentiments which ran counter to those generally found in Mendeleev's writings it is very unlikely that Mendeleev would have retained it throughout 8 editions, spanning more than 35 years, unless it reflected an actual inconsistency or confusion in his ideas. And even if we were to accept the possibility of the existence of such inconsistency or confusion for the period prior to the late 1890's, Mendeleev's explicit rejection in 1898 of a positivistic interpretation of the concept "element" renders it inconceivable that he should not then have

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[42] Brockhaus-Efron, Bibl.11, vol.23, half-vol. 45, p.312 (PLBA, 240). Mendeleev's criticism here of positivistic attitudes is not directed against any particular person.

A similar anti-positivistic argument to that expressed by Mendeleev, based on the evidence of the success of the periodic law, has been given by F.A. Paneth (Bibl.89, p. 152): "If it is maintained that the elements are not present in their compounds in actuality ... but only potentially (as simple substances), then the fact that the properties of their compounds can form a basis for the most profound systematics of the chemical elements [sc. the periodic system] becomes inexplicable".

[43] Pr.Ch., R-1: Colls., 13, 73-4. Similar passages occur in subsequent editions of Pr. Ch. (see above).

revised the passage for the 7th (1902-3) and 8th (1906) editions of Principles of Chemistry.[44]

On the basis of the above considerations I am inclined to reject a positiviatic interpretation of this passage which F.A. Paneth has seen as showing Mendeleev's "predilection for the erroneous [positivistic] view of Ostwald". Instead, I feel that in this passage Mendeleev is talking solely in terms of simple substances not as a "concession" to the view that the concept of "element" is restricted to that of "simple substance" only, but merely to point out the conclusions which follow if such an assumption is in fact made. That he himself recognised a broader significance for "element" is then made clear in the text immediately following the passage in question.[45]

The properties which Mendeleev attributed to the chemical elements (i.e., to the persisting material components of the simple substances and compounds) comprised the quantitative properties of atomic weight and valency (or "atomicity"), and a whole series of largely qualitative properties representing generalisations of the particular physical and chemical properties of the simple substances and compounds into which the elements enter, such as tendency to form acids or bases, degree of stability

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[44] This argument can of course be met by resorting to explanation in terms of an "inertial effect" which carries redundant or obsolete passages through to later editions of a book. However, explanation by such an "inertial effect" in this case is weakened by the fact that for the 7th edition Mendeleev did revise other parts of the very paragraph in which the passage in question is found.

[45] As an extension of the above consideration of whether or not there was a certain hint of positivism in Mendeleev's doctrine of the chemical elements, we might consider the question of what positivistic or agnostic tendencies Mendeleev may have shown in a broader context. Of some relevance to this question would seem to be Mendeleev's attitude towards the writings of the chemist C. Gerhardt (1816-1856) and of the philosopher August Comte. On the basis of the rather scant evidence available, R.B. Dobrotin (Bibl.16, pp.106-115) has concluded that although Mendeleev was strongly influenced by Gerhardt's "unitary" theory it was not the agnostic aspects of this theory (with respect to molecular structure) which influenced him, but rather Gerhardt's concept of "molecule"; and that Mendeleev rejected the positivism of Comte. While Dobrotin's conclusions seem on the whole to be justified, there is one passage in Principles of Chemistry - first occurring in R-6 (1895) 422, and found also in R-7 (1902-3) and R-8 (1906) - where in a discussion of dimorphism Mendeleev appears to suggest, somewhat after the fashion of Baudrimont, Laurent and Gerhardt, that we cannot with any confidence infer molecular structure from chemical reactions, because chemical reaction involves movement of the atoms away from their arrangement in the unreacting molecule (see later, section C of this chapter). Finally, we note that in the 7th and 8th editions of Pr.Ch. Mendeleev seems to pay lip-service (but no more) to a Kantian type of agnosticism when he writes, "Substances can be studied only according to their properties or their relations to our organs of sense and to other substances and bodies, but in itself (samo po sebe) matter is beyond the grasp of our understanding; for there is something in its nature which is self-existent (samobytnoe) and foreign to our understanding and spirit" (Colls., 24, 90; see also Pr.Ch., E-3, 1905, I, p.3, n.2).

of compounds, metallic or non-metallic character in the free state (as simple substances), and so on.[46]

Atomic weight was considered by Mendeleev not to be necessarily dependent upon the atomic-molecular theory for its significance. In fact he once suggested, in line with this view, that "by replacing the term 'atomic weight' with the term 'elemental weight' (elementarny ves) we could avoid the notion of atoms when talking about the elements".[47] Because atomic weight seemed to provide the only unique quantitative characterisation of the different chemical elements this property was seen as especially significant by Mendeleev,[48] its significance being enhanced for him by the discovery of the periodic dependence upon atomic weight shown by the other properties of the elements.

Although Mendeleev recognised valency (valentnost' or atomnost') also as a fundamental property of the elements, he was at the same time critical of a number of aspects of what he called the "doctrine of atomicity". These criticisms tended to be variations on two main themes: first, he criticised theories which adhered to the idea of a fixed (single-valued) valency for each element; and secondly, he criticised the "structuralist" approach which incorporated the idea of valency into a conception of molecules as internally-static structures.[49] However, not only did Mendeleev accept the idea of valency as a variable (many-valued) property of the elements, but his work on the periodic law actually consolidated the notion of valency - notably in connection with the significance of maximum valency with respect to oxygen in "saline" ("non-peroxide") oxides, and in connection with the numerical relation between valencies with respect to oxygen and hydrogen.[50]

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[46] For a discussion by Mendeleev of the different types of property characteristic of the chemical elements see especially his paper in Liebig's Annalen, 1871, pp.134-6 (PLBA, 102-4) and that in Brockhaus-Efron, Bibl.11 1898, pp.312-5 (PLBA, 241-8).

[47] Liebig's Annalen, 1871, 136: PLBA, 104; Sc.Ar. 348-349.

[48] See, for example, PLBA, 17 (1869).

[49] Mendeleev's criticism of theories of fixed (single-valued) valency, such as the "chain theory" and the "molecular compound theory" (the latter of which incorporated also an element of "dualism", which was quite alien to Mendeleev's "unitary" view of the molecule), was at its height at around 1870, when the idea of variable (many-valued) valency was already becoming widely accepted (see especially his paper in Liebig's Annalen, 1871, pp. 211-229; PLBA, 161-176); his anti-structuralist tendencies seem to have reached their peak during the 1880's (see, for example, his Royal Institution lecture of 1889, given as an appendix in all three English editions of Pr.Ch.; for a Russian version, see PLBA, 529-554). For an account of the history of valency in general, see Russell, Bibl.100.

[50] Those contributions by Mendeleev to the development of the notion of valency are considered later, in Chs. III and V.

C. Mendeleev's version of the atomic-molecular theory.

Mendeleev's version of the atomic-molecular theory possessed the following two fundamental characteristics -

i) It was a dynamical theory, not allowing static arrangements of atoms: molecules for Mendeleev, unlike the "structuralist" organic chemists such as Butlerov, were systems of atoms in a state of mobile equilibrium, not static arrangements of atoms held together by fixed, spatially-directed bonds.[51]

ii) It considered all natural phenomena to be manifestations of matter in motion - either visible, macroscopic motion, or some kind of "inner" (atomic-molecular) motion. For example, in referring to electrical and chemical phenomena Mendeleev wrote, "... we should recognise both kinds of phenomena ... as representing different forms of molecular (atomic) motion, whose real nature is not yet understood."[52]

In attempting explanation solely in terms of the various modes and quantities of motion of atoms and molecules Mendeleev's atomic-molecular theory was a reductionist programme for extending the domain of Newtonian mechanics into the "chemical" realm of atoms and molecules. This reductionist aspect of the theory was explicitly acknowledged by Mendeleev, and was claimed by him to represent its "greatest significance":

> The forms and properties of substances are determined by the arrangements of the atoms in space and by their state of motion; and the phenomena accomplished by substances are understood as the shifting of the mutual positions of the atoms, and changes in the motion which we assume them to have. Thus all molecular phenomena... are reduced to mechanical phenomena...[53]

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[51] See especially Mendeleev's Royal Institution lecture 1889, An attempt to apply to Chemistry one of the Principles of Newton's Natural Philosophy, given as an appendix in Pr.Ch., E-1, E-2 and E-3. (Russian version: PLBA, 529-554).

[52] Pr.Ch., R-8 (1906) n.26; Colls., 24, 99.

[53] Pr.Ch., R-1 (1869): Colls., 13, 335-6. Although Mendeleev here, and in certain other passages, lists the "arrangement" (raspolozhenie) and "motion" (dvizhenie) of atoms separately in discussing the nature of molecules, it is clear from an overall survey of his writings that he thinks of "arrangement" under the general category of motion, as an aspect of the "mode of motion" as distinct from the "quantity of motion". See, for example, his Royal Institution lecture of 1889 (op.cit.); and in Pr.Ch., R-6 (1895) 422, n.46 he talks of "... the distribution (motion) of the atoms in the molecules" (also in R-7, R-8).

> ... the very idea of atoms already in its essence reduces the whole of chemistry to mechanics. And in this lies the greatest significance of atomism...[54]

> ... we see in atomism a sublime generalisation in harmony with the fundamental principle of philosophy, namely its direct assimilation of the structure of the universe ... to the composition of matter out of atoms... According to this view a molecule of matter... contains its solitary bodies (atoms) maintained - like the suns and planets - by their proper forces in mobile but stable equilibrium... One of the merits of atomism is that it has brought the extremely small into harmony with the extremely large...[55]

In addition to the merit of the reductionist aspect of his atomic-molecular theory, Mendeleev recognised also two further advantages of the theory -

i) The "simplicity" of the theory: "The atomic doctrine... carries great benefit, because many ideas are then expressed very clearly, briefly and simply".[56]

ii) The atomic-molecular theory provides a model for the doctrine of the chemical elements, explaining the persistence of the elements throughout chemical change; Mendeleev acknowledged that as a result of the atomic-molecular theory, "We have come to learn - and continue all the time to learn - what is conserved in chemical evolutions, and how combinations of invariants undergo changes...".[57] (Mendeleev's interpretation of the doctrine of the elements in terms of the atomic-molecular theory is considered in some detail later in this section).

It must be emphasised that Mendeleev's atomic-molecular "theory" was in fact little more than an outline for a theory - a programme; there still remained the task of establishing the particular nature of the different modes and quantities of atomic-molecular motion corresponding to the various chemical (and other) phenomena.

Mendeleev stressed what we might call the "wholeness" or "integrality"

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[54] 1887: Bibl.73, p.389, n.1.

[55] Pr.Ch., R-8 (1906) n.150; Colls., 24, 101.

[56] Pr.Ch., R-1 (1869): Colls., 13, 340.

[57] Royal Institution lecture, 1889: Pr.Ch., E-3,II, 473; PLBA, 531.

[58] Even in his Royal Institution lecture, where he gives one of his most detailed applications of his version of the atomic-molecular theory, Mendeleev presents no more than a qualitative description of various phenomena (such as valency, isomerism) in terms of his theory. (This point has been made also by Koertge, Bibl.,48, Section Seven: The Periodic Table Case Study, III-C).

of the system of atoms making up a molecule, inheriting this from the "unitary" conception of the molecule to be found in the work of Laurent and Gerhardt (as distinct from the "dualistic" theory of Berzelius, which viewed the composition of the "compound atoms", or molecules, in terms of the electrostatic attraction of two component parts). In his Principles of Chemistry Mendeleev wrote: "... the basis of the entire modern trend in our science... is the unitary doctrine, which shows strict recognition of the joint influence of all elements in a compound body, and denies the pre-existence in them of contrary components... The molecule has been recognised to be a single whole ... We should consider Laurent and Gerhardt as the champions of the unitary doctrine".[59]

Over the course of the years Mendeleev's confidence in the hypothesis of atoms showed an appreciable increase.[60] A prominent aspect of the history of his degree of confidence in this hypothesis was his attitude towards the significance for the hypothesis of the phenomenon of "indefinite" compounds, i.e., compounds (among which Mendeleev included solutions) which do not obey Dalton's laws of constant composition and multiple proportion. During the early part of his scientific career, and even up to the mid-1880's, Mendeleev claimed that the existence of indefinite compounds provided evidence against the atomic theory. Thus, in one of his lectures on theoretical chemistry in 1864 he commented, "At present only the laws of Dalton and Gay-Lussac support the atomic theory ... Certain physical phenomena also speak in favour of the atomic hypothesis. However... in chemistry there exists a whole class of indefinite compounds which, on the contrary, induce us to reject this hypothesis".[61] And in 1869, in the 1st edition of Principles of Chemistry, he wrote, "... the compounds with indefinite ratios ... speak against the atomic doctrine as much as definite chemical compounds speak in its support... Until the atomic doctrine gives

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[59] Pr.Ch., R-8 (1906) n.145.

[60] As indicated earlier however (section A), Mendeleev felt that the atomic theory should be regarded primarily as a "working hypothesis"; he seems to have attached only secondary importance to the question of whether the atomic theory actually represents the "real" structure of matter. Consequently he did not demand "isolation" of atoms as a condition for his supporting the theory. On this question of the "isolation" of atoms (or, strictly, of molecules) Mendeleev wrote in 1876 (Materials for a judgment on Spiritualism (R.): Colls., 24, 197) - "... chemists ... know that they will not get to extract and see these small particles [sc. molecules] in the way that a vegetable cell is extracted".

the possibility of clearly understanding this series of phenomena, we cannot assert that chemistry has given confirmation to this hypothetical idea".[62] Such a view was last expressed by Mendeleev in 1887, in the foreword of his large monograph on solutions; in this instance he referred not to indefinite compounds in general, but to the particular case of solutions - "Solutions constitute a still unsolved great problem of natural science, because, while being chemical compounds, they are not subject to the laws of atomism or multiple proportion ...".[63]

The assertion that the indefinite compounds provide a refutation of the atomic theory is, of course, false, as Mendeleev himself came to realise. Indefinite compounds do constitute counter-examples to the laws of constant composition and multiple proportion, if (as is usual) we take the latter as macro-laws only, but they certainly do not provide evidence against the idea of atoms; we can even save the Daltonian laws of combination if we consider these laws as applying here only at the micro-level (atomic-molecular level).

Mendeleev's rejection of his earlier erroneous view regarding the significance for the atomic theory of the existence of indefinite compounds came with his development of the theory that aqueous solutions are systems of dissociating hydrates - a theory which placed aqueous solutions firmly under the dominion of the atomic-molecular theory. The first detailed account of this theory of solutions was presented by Mendeleev in 1887, in his monograph on solutions. In this work, however, Mendeleev acknowledges that, "The idea of solutions as products of dissociation of definite chemical compounds has been developing in my head for a long time"[64]; and in fact his earliest statement of this idea seems to have been in 1877, in the 3rd edition of Principles of Chemistry - "A solution is a definite compound with water in a state of dissociation".[65] In view of the date of this last remark it is rather surprising that in 1887 Mendeleev could still assert that solutions "are not subject to the laws of atomism".

A particularly clear, and fairly concise, account of his "dissociating hydrate" theory of aqueous solution is given by Mendeleev in the 8th (1906) edition of Principles of Chemistry:

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[62] Pr.Ch., R-1 (1869): Colls., 13, 337.

[63] Bibl.73, p.381 .

[64] Ibid., 385 .

[65] Pr.Ch., R-3 (1877) 149. A survey of Mendeleev's work in the field of solutions has been given by Storonkin and Dobrotin, Bibl.111, and by Mishchenko in Bibl.73, pp.1110-1136.

> The nature of solutions, in the sense of the kinetic hypothesis of matter (i.e., assuming an internal movement of molecules and atoms), may be presented as follows. In a homogeneous liquid, such as water H_2O, the molecules are in a state of mobile but stable equilibrium. When a substance A dissolves in water, its molecules form, with several molecules of water, systems A. n H_2O, which are so unstable that when surrounded by molecules of water they decompose and newly re-form, so that A passes from one group of water molecules to another, and the molecules of water which are at one moment in harmonious motion with A in the form of the system A. n H_2O, at the next moment may have already become free. The addition of water or of molecules of A may either only alter the number of molecules which are free or entering into systems A. n H_2O, or it may introduce conditions for the possibility of the formation of new systems A. m H_2O, where m is greater than or less than n. If the relation of the molecules in the solution should be the same as in the system A. m H_2O, then the addition of further molecules of water or of A would lead to the formation of new molecules A. n H_2O. The relative quantity, stability and composition of these systems or definite compounds will vary from one solution to another. I adopted this view of solutions (in 1887: Pickering subsequently developed a similar view) after a most intimate study of the variation of their specific gravities...[66]

The fact that such a theory shows how solutions, although non-stoichiometric, may nevertheless be seen as obeying the Daltonian laws of combination at the molecular level was pointed out by Mendeleev in the following passage:

> ... the indefinite chemical compounds existing as solutions may ... be brought under the law of multiple proportion by the hypothesis that solutions are unstable hydrates formed according to the law of multiple proportion, but occurring in a state of dissociation... By endeavouring to prove that in solutions we have nothing but the liquid products of the dissociation of definite hydrates, it is my aim to bring also this category of indefinite compounds under the general principle enunciated by Dalton.[67]

The degree of Mendeleev's confidence in the atomic theory after his rejection of the view that the indefinite compounds provide evidence against this theory was clearly expressed by him in 1892:

> Not one authentically-established phenomenon points to the insufficiency of the hypothesis of the independent existence of ponderable atoms of the independent chemical elements. Any other hypothesis, denying the existence of independent chemical atoms of the elements, may only gain some right of citizenship in science when it gives a better understanding of substance, and of the chemical phenomena produced by it, than can be given by the atomic hypothesis.[68]

Another factor which for Mendeleev had some bearing upon the acceptability of the hypothesis of atoms was the question of whether or not the earth's atmosphere has a limited extension into space. The argument that an atmosphere of finite extent indicates a finite divisibility for

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[66] Pr.Ch., R-8 (1906) n.86; Bibl. 73, pp.1102-3.

[67] Pr. Ch., R-6 (1895) Ch.IV, n.30.

[68] Brockhaus-Efron, Bibl.11, vol.6, half-vol.11, 1892, p.157 (PLBA,569).

matter had been proposed in 1822 by W.H. Wollaston.[69] Mendeleev (acknowledging Wollaston) accepted this argument, and also Wollaston's further view that the discovery of a heavenly body devoid of any atmosphere would provide confirmation of the limitedness of the earth's atmosphere.[70] He first presented Wollaston's argument in a lecture of 1857,[71] and continued to present it in all editions of his Principles of Chemistry (i.e., right up to R-8, 1906).

Before ca. 1870 Mendeleev was inclined to believe in the infinite extension of the earth's atmosphere into space,[72] a belief which did not help to allay the scepticism which he tended to show at this time towards the atomic theory as a result of his views regarding the significance of "indefinite compounds". In the 1st edition of Principles of Chemistry (1869) he wrote, "The atomic doctrine may be acknowledged as a useful hypothesis, but it is not supported by a study of the diffusion of the atmosphere in the universe..."[73] After ca. 1870 Mendeleev came to favour instead the view that the earth's atmosphere extends into space only up to a certain definite limit, largely on the basis of the spectral evidence which indicated that the atmospheres of different heavenly bodies have different compositions, and evidence concerning the motion of comets.[74] He recognised, however, that this evidence was by no means conclusive. On the question of whether there exists any heavenly body without an atmosphere, he confined his specific considerations of this possibility to the case of the moon,[75]

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[69] W.H. Wollaston, On the finite extent of the atmosphere, Phil.Trans. Roy. Soc., 112 (1822) 89-98. Wollaston's argument leads to the conclusion of finite divisibility of matter only if the spontaneous expansion (diffusion) of matter is assumed, as has been pointed out by G. Wilson on p.85 of his paper On Wollaston's Argument from the Limitation of the Atmosphere, as to the Finite Divisibility of Matter, Trans. Roy. Soc. Edinburgh, 1845, 16 (1), pp. 79-86.

[70] On the basis of an observed lack of atmosphere for Jupiter, Wollaston had concluded that "the earth's atmosphere is of finite extent, limited by the weight of ultimate atoms of definite magnitude no longer divisible by repulsion of their parts" (op.cit., 98).

[71] This information is given by the compilers (Makarenia et al.) in Bibl.75, p.67, n.13. I have not personally seen the contents of the lecture in question.

[72] See especially Colls., 15, 431-2, from a lecture given by Mendeleev probably in 1867, but certainly before 1869.

[73] Pr.Ch., R-1 (1869): Colls., 13, 350.

[74] See Colls., 6; and also Researches on Mariotte's law, Nature, 15 (1877) 455-457, 498-500.

[75] Wollaston (op.cit., 91) considered that because of the moon's weak gravitational field any atmosphere would be so thin that it would be difficult to detect; therefore we should concentrate on searching for lack of atmosphere on massive bodies such as Jupiter and the sun. By Mendeleev's time however the moon was the only heavenly body accessible to such an observational search which had still not been shown conclusively to possess an atmosphere.

writing in 1875: "It was once thought that the moon had no atmosphere, but observations by Herschel have indicated the presence of an atmosphere... So far there is no knowledge about the composition of the lunar atmosphere, and therefore the question of the boundary of the earth's atmosphere should be considered as not being solved with any certainty".[76] In the 8th (1906) edition of Principles of Chemistry, he wrote, "... the absence of an atmosphere on the moon, if it were not subject to doubt, would provide a very good confirmation of the atomic doctrine".[77]

Although Mendeleev's change of opinion regarding the significance of "indefinite compounds", and regarding the question of the extent of the earth's atmosphere, led to an appreciable strengthening of his support for the atomic theory over the course of the years, he did not become blind to the possibility of remaining defects of the theory. Thus, in the 7th (1902-3) edition of Principles of Chemistry he drew attention to what he felt to be two defective aspects of the atomic theory. First he criticised the theory on "philosophical" grounds: "I have no doubt that the atomic theory ... has its philosophical defects proper to materialism".[78] His second criticism was of a "scientific" nature: "The radical defect of modern atomism... lies in the vagueness of the conception of the 'ether' which fills both interplanetary and interatomic space".[79]

In 1902 Mendeleev himself presented a tentative solution to the problem of incorporating the luminiferous world-ether into the atomic theory;[80]

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[76] Colls., 6, 590-1.

[77] Pr.Ch., R-8 (1906) n.151; Colls., 24, 104-5; PLBA, 602.

[78] Pr.Ch., R-7 (1902-3) 157, n.30 bis; see also Pr.Ch., E-3 (1905; from R-7), I, 216, n.30a. A possible interpretation of this "philosophical" criticism of the atomic theory is given in footnote 5 of this chapter.

[79] Ibid.

[80] Popytka khimicheskogo ponimaniia mirovogo efira, in Vestnik i biblioteka samoobrazonvaniia, St. Petersburg, 1903, No. 1, 2, 3, 4. A second edition, published as a separate booklet (St. Petersburg), appeared in 1905; unlike the 1903 edition this had a foreword, dated 1st July 1905, but otherwise was unchanged from the earlier edition apart from a few minor and insignificant differences. The second edition, without the foreword, is reprinted in PLBA, 470-517; the foreword is reprinted in PLSM, 542-3. An English translation of the first edition, by G. Kamensky as An attempt towards a chemical conception of the ether, was published as a separate volume (Longmans, London) in 1904, and subsequently included as an appendix in Pr. Ch., E-3 (1905). Apart from omitting the very interesting footnotes of the Russian version Kamensky's translation also omits an appreciable amount of the text, often tending to be more a summary than a rigorous translation.

The periodic tables given in the two editions of Mendeleev's article on the "chemical conception" of the ether which show his placing of the ether (as "x") in the position "0-0" are included in Ch. IV of this thesis, as table 60 (P33) (1903) and table 63 (P35) (1905).

representing the ether as the lightest chemical element - "x" or "newtonium" - with an atomic weight of the order of 10^{-6} (taking H=1), occupying the position "0-0" (i.e., "zero" group, "zero" series) in the periodic table. This "chemical conception" of the ether satisfied Mendeleev's desire to "serve the cause of the unity of science",[81] and provided furthermore an explanation of the inertness of the ether (as a member of the inert-gas family), and an explanation (albeit only qualitative) of the phenomena of radioactivity and the intensification of phosphorescence at very low temperatures; but it failed completely to provide any explanation of the fundamental luminiferous character of the ether. It was emphasised by Mendeleev that "my attempt is no more than a feasible and initial answer to this burning question [sc. of the nature of the ether], its essential object being to bring this question to the fore".[82]

The explanation in terms of his "chemical" ether which Mendeleev suggested for the phenomena associated with radioactivity was that these phenomena arise from disturbances accompanying the entrance and departure of ether atoms into and from embryonic ethereal atmosphere which form in the vicinity of the atoms of the heaviest elements, Ra, Th and U:

> Because uranium and thorium, and also radium ... have the highest atomic weights of all the known elements ..., we should look upon them (like the sun) as being endowed with the highest degree of that individualised attractive capacity (a mean between straightforward gravity and chemical affinity) which determines the absorption of gases, solution, and so on. While conceiving the substance of the world-ether as the lightest of gases x, devoid like helium and argon of the power to form stable and definite compounds, we must not think that this gas is devoid of the faculty of - so to speak - dissolving in or accumulating about large centres of attraction like the sun among the heavenly bodies, and uranium and thorium in the world of atoms. As a matter of fact, direct experiment shows that helium and argon are able to dissolve in liquids, and, moreover, this faculty is individualised, i.e., it depends upon the nature of the gas and of the liquid, and upon the temperature. If ether is the gas x, then surely it must accumulate from all parts of the universe towards the medium or mass of the sun, just as the gases of the atmosphere accumulate in a drop of water. And the lightest of gases x will accumulate also about the heaviest atoms, of uranium and thorium, and perhaps in doing so change its form of motion, like a gas dissolved in liquid. This will not be a definite combination, depending upon a common harmonious motion like the motion of a planet and its satellites, but an embryo of such a combination, resembling the case of a comet in the region of heavenly individualisations; and it may be expected

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Certain aspects of Mendeleev's "chemical conception" of the ether are discussed in detail in Ch.VI, in the section of his extrapolation of the periodic system into the "pre-hydrogen" region.

A brief note in English on Mendeleev's view of the ether has been given by Kargon in Bibl.31.

[81] Pr. Ch., R-7 (1902-3): Colls., 24, 43, n.6.

[82] PLBA, 517.

> more readily for the heaviest atoms, of uranium and thorium, than for those of the lighter (according to atomic weight) elements, just as a comet falling from space into the planetary system goes around the sun, and then once more escapes into space. If such a special accumulation of ether atoms about the molecules of uranium and thorium compounds be admissible, then we may expect peculiar phenomena for these latter, determined by the emission of a portion of the ether held by the molecules..., and by the entry of new ether atoms into their sphere of attraction. It seems to be that the optical and photo-radiant phenomena characteristic of radioactive substances, not to mention their loss of electrical charges, indicate a material flow of something which has not been weighed; and it appears that they may be understood in the way suggested, because peculiar forms of the entrance and egress of ether atoms ought to be accompanied by such disturbances in the ethereal medium as produce rays of light.[83]

Towards the end of the 19th century many scientists, particularly in Britain but also elsewhere, favoured a theory which saw the structure of matter in terms of vortex atoms.[84] In the later editions of his Principles of Chemistry Mendeleev commented upon this theory of vortices:

> In our time there has been laid down the basis of a vortex hypothesis, but it has not been developed; although possibly it has an application in explaining chemical phenomena such an application is not clear, it has not removed the misunderstandings in relation to the space between the rings (similarly, it is not completely clear what is found between the atoms and the planets[85]), and it does not provide an answer to the question of the nature of the moving substance of the rings. It therefore constitutes at present only the germ of a hypothetical conception of the structure of substance, and consequently we see no point in talking about it in detail.[86]

Mendeleev's reaction in the early 20th century to the new ideas of "energetics" (Ostwald) and what he called "electronic" ideas (i.e., those based upon the assumption that electrons are the smallest particles of matter) - ideas which were antagonistic towards, or at least tended to undermine, chemical atomism - was to acknowledge that perhaps chemical atoms do not exist, and if they do exist perhaps they are indeed composite, but until the alternative theories to chemical atomism are more successful than this latter hypothesis we should not reject the notion of individual chemical atoms. Thus, as the 8th (1906) edition of Principles of Chemistry Mendeleev wrote:

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[83] PLBA, 513-4.

[84] The theory of the vortex atom came into vogue in Britain after the publication of James Clerk Maxwell's Atom, in Encycl. Brittanica, 9th edition, Edinburgh, vol.2 (1875). Its popularity began to decline sharply after the discovery of the electron in 1897.

[85] This is a reference to the lack of a clear understanding of the nature of the luminiferous world-ether in the ordinary atomic theory.

[86] Pr.Ch., R-8 (1906) n.151; Colls., 24, 104; PLBA, 601.

> In recent years there has been clearly visible a reaction against this idea [sc. of chemical atoms], from two sides. One side denies substance altogether, ... they say ... substance is only energy ... On the other side against atomism are the supporters of a single "primary" or universal substance, who, with the help of observations of "bombardment" observed with the passage of electricity in extremely rarefied gases, accept unusually small (compared with atoms) "electrons", or material carriers of electric charge. They then either accept the existence of ordinary atoms over and above that of electrons, or the former are considered to be merely aggregates of the latter ... The still very unclear "radioactive" phenomena, and the doctrine of "electrolytic dissociation",[87] play a major role at the base of such "electronic" ideas... But since the usual simple bodies remain in the imagination - not to mention the experience - of even the "energeticists" and the "electronicists", while being completely unexplained in their essence, ... then from a chemical point of view neither of these modern opponents provides any advantage for the understanding of the simple bodies. And if we look at atomism as a scheme which aids the examination of the very great complexity of chemical phenomena, then the great significance of the atomic doctrine cannot be denied. To search for still better, still firmer, truth, is certainly correct, but to dismiss atomism from acceptability in place of something vague should not be done, because behind it are its merits, its history.[88]

Mendeleev's version of the atomic-molecular theory, in representing substances as being composed of materially-invariant atoms in various characteristic states of motion, provided a model both for the material invariance of the elements throughout chemical change (as the material invariance of the atoms) and also for chemical change itself (as change in the state of motion of the atoms). As Mendeleev wrote in 1892, "All atoms of a given element are completely identical to each other, although they are found in very diverse molecules ... The diversity must be attributed only

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[87] Mendeleev did not accept the hypothesis of electrolytic dissociation, believing instead that the phenomena which this hypothesis claimed to explain arose from the dissociation and formation of compounds between the solute and solvent in a solution: "In general I consider the hypothesis in question [sc. of electrolytic dissociation] to be not in accordance with reality ... Above all, I think it well to point out that the nature of solutions certainly seems to be very complex, and there is reason to recognise in them a portion of the substances in a state of combination, and a portion in a state of decomposition, or dissociation, having nothing in common with the still obscure electricity. I consider that it will be necessary to recognise the existence of dissociation and association for the understanding of solutions; and I think that although on the one hand the modern idea of electrolytic dissociation is retarding the progress of the theory of solutions, on the other hand it is useful because it provides a motive for accumulating a store of experimental material which a future theory of solutions must embrace" (Pr.Ch., R-8, 1906, n.71).

[88] Pr.Ch., R-8 (1906) n.151: Colls., 24, 106; PLBA, 603-4.

to the state, circumstances, motion, and in general the relationship of the atoms in the molecules...".[89]

F.A. Paneth, in his discussion of the epistemological status of the chemical concept of "element", has written, "It is only in the formulation 'A chemical element is the class of all atoms of equal nuclear charge' that the chemical element would be defined with complete generality as basic substance [Grundstoff], and no longer as simple substance [einfacher Stoff]"[90] We can correspondingly define Mendeleev's persisting invariant "element", in terms of his own atomic-molecular ideas, as follows: " chemical element in the class of all atoms of equal atomic weight". Since for Mendeleev an atom never occurs in reality without some concomitant motion, "the class of all atoms" will, because of the variety of its concomitant motions, present a corresponding variety of "sensible" manifestations in its simple substances and compounds.

Mendeleev's view of the relationship between the concepts of "element" and "simple substance" ("simple body") on the one hand, and the concepts of "atom" and "molecule" on the other, was outlined by him in the following passage of 1871:

> A simple body is a substance, metal or metalloid, with a set of physical characteristics and chemical reactions. To simple body corresponds the idea of molecule, containing one atom (such as Hg or Cd, and probably also many other simple bodies) or several atoms (S_6, S_2, O_2, H_2, Cl_2, P_4, etc.). It is capable of appearing in isomeric and polymeric forms, and differs from compound bodies only in the fact that its material parts are of the same kind.
>
> By the term element we should understand those material components of the simple and compound bodies which give them their particular collection of physical and chemical properties. To element corresponds the idea of atom.[91]

In 1898 Mendeleev said, "... to the idea of element corresponds the atom, and to simple body the molecule. Simple bodies, like all the bodies of nature, are composed of molecules...".[92]

F.A. Paneth has criticised this suggestion by Mendeleev of a correspondence between the concepts of "element" and "atom", and between

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[89] Brockhaus-Efron, Bibl.11, vol.6, half-vol.11, 1892, p.156 (PLBA 568). (See n.53 of this chapter, and also the quoted passage to which n.57 refers).

[90] Bibl.89, p.151, n.1.

[91] Liebig's Annalen, 1871, 133; Sc. Ar., 344, 345: PLBA, 102.

[92] Brockhaus-Efron, Bibl.11, vol. 23, half-vol. 45, p.312 (PLBA, 240).

"simple body" and "molecule", claiming that "apart from the fact that there are simple bodies whose molecules are single atoms, molecules and atoms belong indubitably to one and the same group of scientific concepts, while the essential difference between element and simple body (in the Mendeleeffian sense of the words) lies in their belonging to quite different spheres in epistemology". Mendeleev's concepts of "element" and "simple body" indeed belong to "quite different spheres in epistemology"; and certainly, as Paneth points out elsewhere also,[94] the concepts of "atom" and "molecule" on the other hand belong to one and the same (viz. the "transcendental") epistemological sphere. But what Paneth appears not to appreciate - and this because he conflates Mendeleev's ideas of "atom" and "monoatomic molecule" - is that within the epistemologically "transcendental" world of Mendeleev's atomic-molecular theory there is an important ontological distinction to be drawn between the concepts of "atom" and "molecule", which mirrors the epistemological distinction between "element" and "simple body". As Mendeleev himself acknowledged (for example, in the above-quoted passage of 1871), there are indeed simple substances whose molecules contain only one atom; but these monoatomic molecules were seen by him as single atoms in that particular state of motion characteristic of the particular simple substance, whereas his conception of "atom" was not tied to any particular state of motion, i.e., to any particular (monoatomic, homopolyatomic or heteropolyatomic) molecule. In Mendeleev's atomic-molecular theory every simple or compound substance is characterised in terms of its molecule, and in this respect the concept of "simple substance" ("simple body") may be said to correspond to the atomic-molecular concept of (monoatomic or homopolyatomic) "molecule"; the atomic-molecular idea of "atom" on the other hand, as a material entity persisting unchanged throughout all molecular processes, corresponds to that of the epistemologically transcendental persisting "element". (It should perhaps be emphasised that although Mendeleev says "to simple body corresponds the idea of molecule", he does not claim the converse, which is of course not true: to the idea of molecule corresponds not merely that of simple body, but also that of compound).

Whereas Mendeleev believed in the real transcendental persistence of chemical elements, he seems not to have believed in any real transcendental persistence of compounds - as compounds, rather than merely as the collection

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[93] Bibl; 90, pp. 57-8.

[94] Ibid., 66: "atom and molecule both belong to the transcendental world".

of their elements - in more complex compounds.[95] For example, he emphasised that when we talk of water being contained in hydrates we are merely using a shorthand to express the facts that water is a reactant in the formation of hydrates, and that it is recoverable from hydrates: "If we say that water occurs in the composition of a certain hydrate, then by this we wish to point out only that there are chemical transformations in which it is possible to obtain that hydrate by means of water, and other transformations in which this water may be separated out from the hydrate. A simple way of expressing all this is to say that water enters into the composition of this hydrate".[96] Such a view is indeed what we would expect from Mendeleev in the light of his atomic-molecular theory. Unlike the case of the persistence of the elements, viewed in this theory as the persistence of the atoms, the persistence of a compound (as a compound, rather than merely as its elements) in a more complex compound would require, according to Mendeleev's atomic-molecular theory, conservation not only of the constituent atoms of its molecule but also of that particular state of motion of these atoms which is characteristic of its molecule. But it is hardly feasible that Mendeleev's "unitary" conception of the molecule could allow that the state of motion of the atoms in any molecule might remain unchanged when this molecule becomes an integral part of the system of atoms of a more complex molecule. In connection with this point, there is one passage among Mendeleev's writings where he is not even prepared to acknowledge that molecules necessarily retain their identity in a change from one polymorph to another:

> Dimorphous bodies are distinguished from actual isomers and polymers because no differences are observed in their chemical reactions, ... and therefore dimorphism is usually ascribed to a difference in the arrangement[97] of the similar molecules which build up the crystals. Although such an hypothesis is fully possible in the spirit of the atomic-molecular doctrine, yet, because we cannot assume complete conservation of the arrangement of the atoms within the molecules when the molecules themselves are in different arrangements, and because in every attempt at chemical reaction there must occur a certain motion among the atoms, then in my opinion there is no solid basis for

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[95] The general questions of the real transcendental persistence of "compounds of the first order" (e.g., SO_3 and H_2O) in "compounds of higher order" (e.g., H_2SO_4), and of organic radicals, have been considered by F.A. Paneth, Bibl. 89, pp. 156-7.

[96] Pr.Ch., R-7 (1902-3), R-8 (1906), Ch.I; Kamensky's translation is given in E-3 (1905; from R-7), I, 109.

[97] Earlier in this very passage Mendeleev indicates that when he talks of the "arrangement" of the atoms in the molecule he is referring to their state of motion: he talks of "the arrangement (motion) of the atoms in the molecules". (See n.53 of this chapter).

separating dimorphism from the general conception of isomerism.[98]

As regards Mendeleev's attitude towards the question of the "pre-existence" of compound radicals (as opposed to the "simple radicals" or elements) in molecules - i.e., of the real transcendental existence of radicals as particular dynamical systems of atoms, not merely as the collection of their atoms - there is insufficient evidence to support any definite conclusion.[99] We note merely that in terms of Mendeleev's atomic-molecular theory such pre-existence is not as readily dismissible as is the persistence of molecules in more complex molecules: whereas according to Mendeleev's atomic-molecular theory persistence of a molecule within a more complex molecule demands unacceptably the absence of influence of the remainder of the more complex molecule upon the "persisting" molecule within it, pre-existence of radicals demands the rather more plausible equivalence of influence of the varying part of the molecule upon the unchanging part (the radical) for the series of molecules in question.

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[98] Pr.Ch., R-6 (1895) 422, n.46; also given in R-7 (1902-3) 439, n.46, and R-8 (1906) n.389. This passage seems to contain the argument - first presented by A.E. Baudrimont in his Introduction à l'Étude de la Chimie par la Théorie Atomique, 1833 - that chemical reactions are not a reliable indication of molecular structure because reaction necessarily involves movement of the atoms away from their arrangement in the unreacting molecule. This is a view which I have not found expressed elsewhere by Mendeleev. (See n.45 of this chapter).

[99] The existence of "free radicals" is ignored here. To discuss such entities in connection with Mendeleev's views would in fact be largely anachronistic. (The relatively long-lived free radical triphenylmethyl was discovered in 1900, by Gomberg; short-lived aliphatic free radicals were first prepared and detected in the late 1920's, by F.A. Paneth and Hofeditz).

CHAPTER II

MENDELEEV ON THE QUESTIONS OF PRIMARY MATTER AND THE COMPLEXITY OF THE CHEMICAL ELEMENTS

A. Introduction

Although there is certainly an overlap of the concepts of a single primary matter and complexity as applied to the chemical elements, these concepts do not overlap completely in this context. This fact is illustrated in the scheme given below, in which the nature of the elements is considered from the point of view of the nature of the corresponding chemical atoms: the concept of a single primary matter is denoted by the letter Σ, and that of complexity of the elements by the letter K[1] -

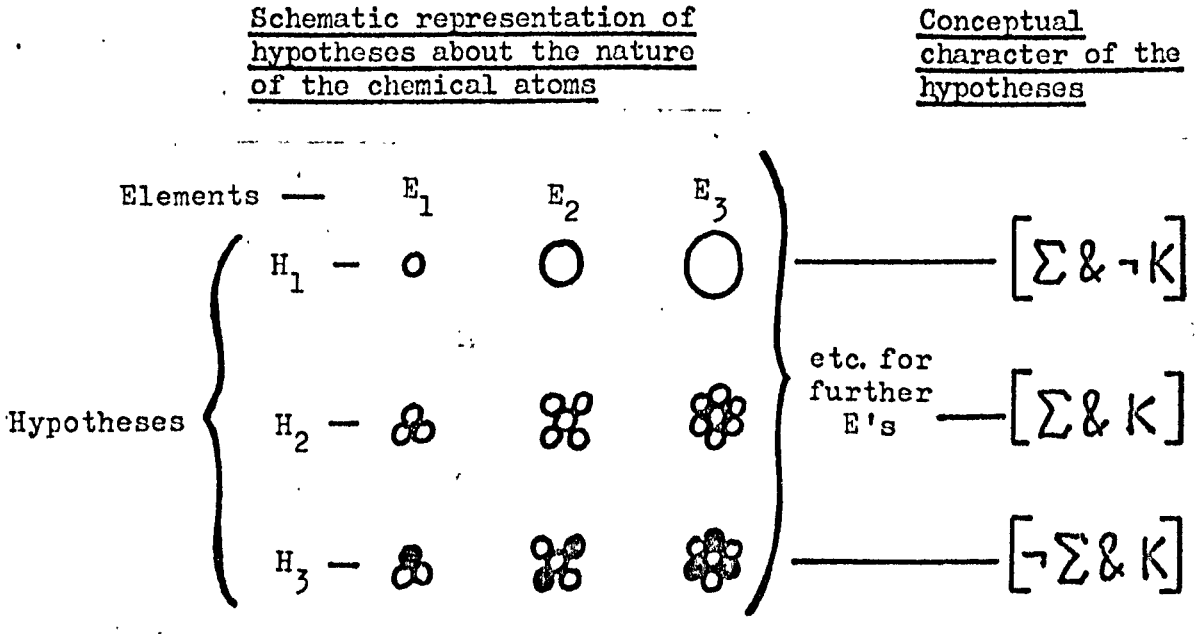

Fig.II-1.

Within each row in this scheme, circles of the same shading denote ultimate atoms composed of qualitatively the same matter, different shading denoting qualitatively different matter (i.e., unshaded circles represent one kind of primary matter, shaded circles another kind). Circles of the same size and same shading represent ultimate atoms of an identical type.

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[1] In this scheme the symbol "&" denotes conjunction, and "¬" denotes "not".

In addition to the above three types of hypothesis, there are other possible related hypotheses which represent some sort of hybrid of H_1, H_2 and H_3. For example, there is the following hybrid of H_1 and H_2 -

E_1 E_2 E_3 } etc. for
o ♣ ⌘ } further E's,

which is conceptually of the type, $\Sigma \,\&\, [K \vee \neg K]^2$; this particular type of hypothesis has an historical significance in connection with the speculations of William Prout (see later).

Among the various grounds upon which were founded the 19th-century and early 20th-century theories of primary matter and the complexity of the elements we can distinguish "philosophical" grounds, which comprise a priori demands for unity and simplicity in nature, and "empirical" grounds, among which we include not only those empirical observations which were considered (at least by some scientists) as providing direct corroboration of a particular theory, but also certain empirical data which were considered to provide analogical support for a given theory.[3]

A desire for unity and simplicity had been evident in conjectures about the nature of the material world from classical times onwards. In 19th-century science a particular influence in encouraging this tendency was provided to some extent by the German movement of Naturphilosophie (Goethe, Schelling) of the early part of the century, a movement which stressed the connectedness of nature. Moreover, the state of chemistry during the 19th century was such - with its 50 or more "simple substances" - that it seemed to pose an especially serious threat to the demand for unity and simplicity in the material world. It was undoubtedly largely on the basis of an underlying desire for some sort of unity of matter that the Proutian-type conjectures of the 19th century persisted, with certain ad hoc modifications, in the face of a series of apparent empirical refutations.

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[2] "v" denotes "or".

[3] Although such "analogical" support for theories of primary matter and the complexity of the elements is here included under the general heading of "empirical" grounds because it involves drawing analogy from particular empirical data, it should be noted that the very basis of all such analogical reasoning is the "philosophical" belief in, or desire for, an overall unity or connectedness in nature.

The various kinds of ("direct" and "analogical") empirical ground upon which theories of primary matter and the complexity of the elements were founded in the 19th century may be classified into the following scheme:-

a) Numerical relationships between the atomic weights of the elements: simple commensurability of atomic weights; and numerical relationships between the atomic weights of chemically-similar elements.

b) Decomposition, synthesis and transmutation of the elements.

c) Analogy of the elements with compound radicals (both inorganic and organic) and with organic compounds.

d) The periodicity of the properties of the elements.

e) Spectroscopic data.

f) Other, miscellaneous, empirical grounds.

These classes are not entirely mutually exclusive. Nevertheless, this classification provides a convenient framework within which to discuss the 19th-century and early 20th-century views on primary matter and the complexity of the elements.

Before discussing the views of Mendeleev himself we shall attempt (section B) to give some idea of the intellectual climate of the scientific world in which he worked: broadly speaking, this climate seems to have been favourable towards the ideas of the unity of matter and the composite nature of the elements, increasingly so as the years passed. Mendeleev's own views (presented in section C) will be seen to be in certain significant respects less favourably disposed than those of the majority of his contemporaries towards the ideas of primary matter and the complexity of the elements, although his attitude was by no means one of such complete rejection of these ideas as has sometimes been suggested.

B. Views on primary matter and the complexity of the elements which were held by scientists other than Mendeleev in the period from the early 19th century to the early 20th century.[4, 5]

A "philosophical" ground for belief in the complexity of the elements can be recognised in Dumas' comment of 1869, "We are inclined to think Lavoisier's elements further reducible from considering ... their number, which has risen in less than a century from thirty-one to sixty-five, and which grows rapidly."[6] Lord Rayleigh, in 1882, referred to "the a priori argument in favour of simplicity"[7] in connection with Prout's hypothesis that the atomic weights of the elements are integral multiples of that of hydrogen. And Lothar Meyer, writing in 1884, said: "the existence of some sixty or even more fundamentally different kinds of primordial matter is intrinsically not very probable".[8] There are many other examples which could be cited to illustrate the importance of the "philosophical" ground in stimulating and supporting theories of primary matter and the complexity of the elements in the 19th century and early 20th century. But over and above such underlying "philosophical" grounds were the various empirical grounds which served to remove the theories in question from the realms of mere speculation into the realm of science.

a) Views based upon numerical relationships between the atomic weights of the elements.

A prominent aspect of 19th-century and 20th-century views on primary matter and the complexity of the elements was"Prout's hypothesis" and its

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[4]We shall consider the period up to ca.1905, just before Mendeleev's death.

[5]Much important primary material relating to this topic has been reprinted in Bibl.47 (compilation and comments by D.M. Knight, 1970). A survey of 19th-century views on "The ultimate constitution of matter and the genesis of the elements", with many quotations from primary sources, is given by Ida Freund in The study of chemical composition. An account of its method and historical development, 1904, Cambridge Univ. Press (republished 1968, Dover Publications, New York), Ch. XIX. Other secondary sources on the subject include those by Farber, 1964 (Bibl.19), W.V.Farrar, 1965 (Bibl.20), and Knight, 1967 (Bibl.46).

[6]Faraday Lecture, 17th June 1869: Chem. News, 20 (1869) 3.

[7]British Association address: Chem. News, 46 (1892) 97.

[8]Die modernen Theorien der Chemie, 5th edn. (1884), 134. Given in Bibl. 90, p.56.

modifications.[9]

A number of distinct but related hypotheses have been designated "Prout's hypothesis" or "Prout's law", or recognised as modifications of "Prout's hypothesis". A fundamental distinction in this respect is between what we might call "commensurability" hypotheses and "protyle"[10] hypotheses: the former are those which postulate some sort of simple commensurability of the atomic weights of the elements; the latter are those which claim that the chemical atoms are all built up from "sub-atoms" of primary matter, or "protyle".[11] The history of "Prout's hypothesis" concerns not only a series of commensurability hypotheses but also a series of corresponding protyle hypotheses. Among the Proutian-type commensurability hypotheses variety arises in the choice of the particular weight-unit of which all atomic weights are considered to be integral multiples; the Proutian-type protyle hypotheses vary according to the particular building-unit (i.e., protyle atom) postulated.

The various types of Proutian commensurability and protyle hypotheses may be conveniently denoted by using the abbreviations PCH and PPH respectively for "Proutian commensurability hypotheses" and "Proutian protyle hypothesis", and indicating in parentheses either (for a PCH) the weight-unit of which all atomic weights are considered to be integral multiples, together with the atomic-weight standard, or (for a PPH) the postulated structural building-unit:

Proutian commensurability hypotheses	Corresponding Proutian protyle hypotheses
PCH $(\frac{1}{n};\ H = 1)$	PPH $(\frac{1}{n}\ H)$
PCH $(\frac{1}{n};\ O = 8$[12], or $O = 16)$	

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[9] "Prout's hypothesis" is the subject of Bibl.95. A brief survey of the history of "Prout's hypothesis" is given by O.T. Benfey, J.Chem.Ed., 29 (1952) 78, and by Farrar, Bibl.20. W.H. Brock discusses (among other things) the history of "Prout's hypothesis" up to 1850 in Bibl.10.

[10] From the Greek πρωτη ὑλη ("first matter"). Prout (1816) used the Greek expression; the English word "protyle" was popularised by W.Crookes in the 1880's.

[11] Such a distinction has already been pointed out by W.H. Brock in Bibl.10, and in his paper "Dalton versus Prout : the problem of Prout's hypothesis" in John Dalton and the progress of science, ed. D.S.L. Cardwell, Manchester Univ. Press, 1968. Brock distinguishes Prout's "integral multiple weights hypothesis" or "multiples hypotheses" from his "protyle hypothesis" or "unitary hypothesis".

[12] Before the 1860's the atomic weight of oxygen was commonly taken to be the same as its equivalent weight.

The specific historical cases which are encountered had n=1[13], n=2, n=4, and various values of n very much greater than 4.

The Proutian commensurability hypotheses possessed scientific significance only insofar as they postulated the existence of a commensurability of atomic weights which was empirically testable. Those with n=1, 2 or 4 were all scientifically significant in this sense, although to a lesser extent the smaller the postulated weight-unit (i.e., the larger the value of n). On the other hand, the actual historical examples of commensurability hypotheses with $n \gg 4$ were certainly outside the realms of science (at least, of the science of the time). Whereas the "scientific" commensurability hypotheses with n=1, 2 or 4 were postulated - on the basis of an examination of experimental atomic-weight values - prior to any corresponding protyle hypothesis, the hypotheses with $n \gg 4$ represented corollaries to prior-formulated protyle hypotheses. As examples of the latter we have de Boisbaudran's suggestion (1895) that the atoms of the elements may be built up of sub-atoms whose weight is as little as $\frac{1}{128}$ that of the hydrogen atom,[14] and Zängerle's conjecture (1882) that the hypothetical universal ether, with an atomic weight $\frac{1}{1,000}$ that of hydrogen, is the protyle of all the chemical elements.[15] Zängerle's suggestion provoked the response from Lothar Meyer and Karl Seubert that, "Speculations of this kind are far removed from any possibility of experimental proof, and can therefore never be expected to receive from it any support."[16]

It was commonly accepted in the period under consideration that the confirmation of a given testable PCH would provide strong evidence in support of the corresponding PPH, e.g., that confirmation of PCH (1; H=1) would strongly indicate the truth of PPH (1H), the hypothesis that all chemical atoms are built up of hydrogen atoms.[17] However, the eventuality

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[13] It was the hypothesis PCH (1; H=1) which was most usually referred to as "Prout's hypothesis" before the late 19th century; after this, the term came to be used commonly also for PCH (1; O=16). The hypothesis PPH (1H) was also sometimes designated "Prout's hypothesis".

[14] Comptes rendus, 120 (1895) 1097; a summary is given in Chem. News, 71 (1895) 271.

[15] "Über die Natur der Elemente, Progr. des königl. Realgym. München, 1882. (See Venable, Bibl.124).

[16] Berichte der deutschen chem. Ges., 18 (1885) 1097-1104.

[17] A notable exception to this generalisation appears to have been provided by Thomas Thomson (see below). Thomson's attitude in this respect is discussed by Brock in Bibl.10.

Another exception was provided by Berthelot (Les Origines de l'Alchimie, Paris, 1885, 313), who considered that confirmation of a PCH would not

of refutation (be it "partial" or "complete" - see below) of such a commensurability hypothesis was regarded by a number of scientists as not necessitating refutation of the corresponding protyle hypothesis, the latter being saved in this case by the ad hoc postulation that the weight of a chemical atom may be different from the sum of the weights of its constituent protyle atoms.[18]

Much of the history of Proutian-type conjectures from the middle of the 19th century to the beginning of the 20th century is concerned not with the situation where there is a seemingly clear-cut confirmation or refutation of a particular PCH, but rather with cases where although there is no complete confirmation, there nevertheless appears to be a significantly closer correspondence of the atomic weights to the values demanded by a particular testable PCH than would be expected on the assumption of a random distribution of atomic-weight values over the appropriate range of real numbers.[19] Many scientists of this period, on the basis of such "probability" considerations, refused to reject the PCH in question while at the same time accepting the accuracy of the experimental data[20]: some of these scientists went no further than expressing their belief in the unlikelihood

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lead him to believe in the corresponding protyle hypothesis (where the elements are thought of as aggregates of protyle atoms), but rather to believe that the elements represent quantitatively different homogeneous condensations from a single primary matter. In the notation used in section A, Berthelot's suggestion is of the conceptual type $[\Sigma \,\&\, \neg K]$.

[18] Among those who suggested the possibility of a breakdown of the law of conservation of weight for the building of chemical atoms from protyle atoms were Marignac (1860: see later), Mendeleev (1871: see Ch.I, and later in the present chapter), A.D. Risteen (The molecular theory of matter, Boston, Mass., 1896, p.160), and G. Rudorf (1900: see later). Lothar Meyer (Die modernen Theorien der Chemie, 6th edn., Breslau, 1896, Book 1, p.124) made another suggestion: "It is conceivable that the atoms of all or of many of the elements are essentially composed of smaller elementary particles of one primordial matter, perhaps of hydrogen, but that their weights do not appear as rational multiples of each other because in addition to the primordial particles, greater or smaller amounts of ... luminiferous ether, which may not be devoid of all weight, may enter into the composition of atoms".

[19] Those who actually calculated probabilities in this connection include Mallet (1880), Strutt (1901), Rudolph (1901) and Marshall (1902) (see later). Certain modern commentators, for example W.F. Farrar (Bibl.20, p.310) and D.M. Knight (Bibl.47, pp.12 and 350), have claimed that Augustus de Morgan, in a letter to W.H. Gladstone published in a paper by the latter (Phil. Mag., 4th series, 5, no.33, May 1853, 313-20) gave a calculation of the probability that the atomic weights should approach as closely as they do to whole numbers as a result of "chance". This is incorrect; what de Morgan calculates in this letter is the probability that 60 random selections (with repetition allowed) from 100 given (different) numbers will result in the selection of some one unspecified number at least 6 times, this calculation being related by Gladstone to the clustering of empirical atomic weights about certain values.

[20] As might be expected, there were also those who refused to reject a PCH which was contradicted by experiment, on the grounds that the experimental data were probably wrong, e.g., Odling (1863) shows this tendency (see later).

of an "accidental" approach of the atomic weights so closely to the values demanded by the PCH;[21] others suggested that under certain special experimental conditions strict commensurability would perhaps hold.[22]

The history of "Prout's hypothesis" begins with the publication of two anonymous papers in the Annals of philosophy (ed. Thomas Thomson) in 1815-16[23]. Within a few months of the appearance of the second paper it was made known by Thomson that the author was Dr. William Prout. Prout's 1815 paper contained, in somewhat indirect form, the commensurability hypothesis PCH (1; H=1);[24] in his 1816 paper Prout proposed, as a tentative corollary to this, the protyle hypothesis PPH (1H) - "If the view we have ventured to advance [sc. PCH (1; H=1)] be correct, we may almost consider the πρώτη ὕλη of the ancients to be realised in hydrogen; an opinion, by the by, not altogether new".[25]

Prout's conjectures soon had many adherents, although mainly in England. The principal advocate of PCH (1; H=1) was Thomas Thomson.[26] However, unlike most adherents of PCH (1; H=1) Thomson seemed reluctant to accept Prout's protyle hypothesis, PPH (1H), even though he did not believe the chemical elements to be ultimate.[27]

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[21] For example, Strutt, 1901 (see later).

[22] For example, de Chancourtois, 1862, and Butlerov, 1881-2 (see later).

[23] On the relation between the specific gravities of bodies in their gaseous state and the weights of their atoms, Ann. Phil., 6 (1815) 321-30 and 472, Correction of a mistake in the essay on the relation between the specific gravities of bodies in their gaseous state and the weights of their atoms, Ann. Phil., 7 (1816) 111-13. Reprinted in Bibl.95.

[24] "I had often observed the new approach to round numbers of many of the weights of the atoms, before I was led to investigate the subject" (op.cit., 330; Bibl.95, p.36).

[25] Op.cit., 113; Bibl.95, p.40. The final comment in this passage is probably an acknowledgment of the views expressed by Humphry Davy on the possibly primary nature of hydrogen: see, for example, Davy's Elements of Chemical Philosophy, 1812, pp.274-5.

[26] Having presented the hypotheses PCH (1; H=1) and PPH (1H) in 1815-16, Prout himself played no part in popularising and defending these hypotheses in their early years. He appears not to have commented upon such subjects again until the 1830's (see below).

[27] Brock, Bibl.10, p.310 quotes the following passage from Thomson's An Attempt to Establish the First Principles of Chemistry by Experiment, London, 1825, vol. 1, p.31: "All our simple bodies are most probably compounds. It is possible that the ultimate elements of bodies may be very few - it is even conceivable that they may be reduced to two; but in what way all the variety of bodies with which we are acquainted, could be produced from one single kind of elementary body or atom, I cannot, for my own part, form any conception".

Shortly after the appearance of Prout's 1815 paper, J.L.G. Meinecke began to publish a series of articles on stoichiometry. In the second of these he wrote, "... according to Dalton all stoichiometrical magnitudes are multiples by whole numbers of the value of hydrogen";[28] and in the following year he remarked, "It is noteworthy that the number of hydrogen is a divisor of the remaining stoichiometrical numbers".[29] Meinecke did not mention Prout in any of his publications, although he was considered to have been aware of Prout's contribution. Thomson, in 1818, wrote, "I ... suspect Meinecke has been influenced by Prout's paper, though he has taken no notice of it".[30]

Prout's commensurability hypothesis apparently received a not unfavourable initial reception from Berzelius.[31] However, the results of his own atomic-weight determinations soon turned Berzelius against the hypothesis; by the early 1820's he was clearly its most prominent opponent, his antagonism in this respect being directed mainly against Thomson.[32] Because of Berzelius' great standing on the Continent, European chemists in general tended to support him at this time in his opposition to PCH (1; H=1).[33]

The 1830's saw a fading of the support for PCH (1; H=1) in England, hitherto the stronghold of this hypothesis.[34] In 1829 Edward Turner, then

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[28] Annalen der Phys. (Gilbert), 24 (1816) 162. There is very little evidence to support Meinecke's claim that Dalton had believed the "combining weights" of all elements to be integral multiples of that of hydrogen. It is possible that Dalton held such a view briefly, in 1808, but even this is doubtful; certainly he held no such view in 1804 and 1810. (On this question see Bibl.95; and O.T. Benfey, op.cit.).

[29] J. für Chem. (Schweigger), 22 (1817) 138.

[30] Ann. Phil., 12 (1818) 10.

[31] According to Venable, Bibl.124, p.22.

[32] In 1821, in a letter to Gaspard de la Rive, Berzelius made the following derogatory remark about the principal advocates of the two kinds of atomic-weight relationship being proposed at the time (viz. PCH and the "triad-relationship"): "Thomson has no common sense in chemistry. I do not know whether he or Döbereiner in Germany is the worst chemist existing at this moment" (see Bibl.92, p.225). In 1827 Berzelius wrote of Thomson's An Attempt to Establish the First Principles of Chemistry (1825) that it "belongs to those few productions from which science will derive no advantage whatever. Much of the experimental part, even of the fundamental experiments, appears to have been made at the writing-desk; and the greatest civility which his contemporaries can show its author, is to forget that it was ever published" (Jahresbericht, 1827, p.77; a translation into English by Wöhler is given in Phil.Mag., 2nd series, 4, 1828, p.451).

[33] Later however, around 1840, PCH (1; H=1) was to gain some appreciable support in France (see below).

[34] Even Thomson had become somewhat reticent on this subject by this time, as may be seen from his History of Chemistry (1831-2).

an adherent of the hypothesis, began a revision of Thomson's atomic-weight determinations.[35] By 1832-3 his research had led him (and many other English chemists) to reject Thomson's results, and with them PCH (1; H=1).[36] The results of experiments by Frederick Penny in 1839 added to the evidence against PCH (1; H=1)[37].

In the meantime Prout himself had made certain comments during the 1830's in connection with the composition of the chemical atoms and the commensurability of atomic weights. In 1831, in a letter to Daubeny, he wrote: "... as the atom of hydrogen, the lowest body known, is frequently subdivided when in combination with oxygen, etc. there seems to be no reason why bodies still lower in the scale than hydrogen ... may not exist, of which other bodies may be multiples, without being actually multiples of the intermediate hydrogen."[38] In this passage we find the idea of "fractional chemical atoms" (arising, apparently, from a failure on Prout's part to recognise the existence of polyatomic molecules of simple substances) being used as an argument for the composite nature of the elements. This suggestion by Prout of the possibility that sub-multiples of hydrogen are the units from which all the elements are built comes ten years before Marignac's suggestion of $\frac{1}{2}$ H as a unit, and more than 25 years before Dumas' suggestion of $\frac{1}{4}$ H (see later).[39]

In 1834 Prout had the following to say on the question of the empirical testability of hypotheses which postulate a simple commensurability of atomic weights: "The matter is one that in the present imperfect state of chemistry can hardly be determined by experiment; for what with the difficulty, or

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[35] Turner was professor of chemistry in the University of London.

[36] In Sept. 1831, at the first meeting of the British Association, it had been recommended that PCH (1; H=1) be checked in the case of certain elements. At the second meeting, 1832, Turner presented some results on this question which were published in Phil. Mag., 3rd series, 1 (1832)109-12. A full report of his work in this field was communicated by Turner to the Royal Society in 1833: Phil. Trans. Roy. Soc., 1833, pp. 523-39. A few chemists criticised Turner's results, e.g., Phillips, Phil. Trans., 1839, p.35; Phillips had found Cl=36, compared with Turner's Cl=35.31.

[37] Phil. Trans., 1839, pp.13-33. Penny was a professor at Glasgow; he had, prior to 1839, been a supporter of PCH (1; H=1).

[38] Published as an appendix in Daubeny's On the atomic theory, 1831, pp. 129-30.

[39] Unlike the case of Prout, there is no reason to believe that Marignac and Dumas postulated units of $\frac{1}{2}$H and $\frac{1}{4}$H on the basis of the "fractional-atoms" fallacy; in fact, all indications suggest that they appreciated the idea of polyatomic molecules of simple substances.

rather impossibility, of procuring bodies in a perfectly isolated form, and the unavoidable imperfections of all chemical processes, we can scarcely hope to arrive within the necessary limits of precision."[40]

While the end of the 1830's found PCH (1; H=1) out of favour with most English chemists, the hypothesis began at this time to receive some appreciable support in France. This arose out of Dumas' re-determination in 1839-40 of the atomic weight of carbon. Dumas, assisted by his pupil Stas, found the C:H ratio to be exactly integral,[41] a result which prompted him to write, "If, as Dr. Prout thought, and as now seems highly probable, all the atomic-weights are integral multiples of that of hydrogen, there will be many matters to set right among the accepted atomic weights. Later experiments will decide this point; but it is evidently necessary now to submit it to serious verification".[42] Dumas (assisted to some extent by Stas) went on to find an integral ratio also for O:H.[43]

The results of Dumas and Stas were confirmed by Erdmann and Marchand.[44] However, although these experiments revived interest in, and support for, the hypothesis PCH (1: H=1), there remained the notable stumbling-block of the atomic weight of chlorine (=35.5). To overcome this problem (and similar problems posed by certain other elements) Marignac suggested that the atomic weights of the elements are all integral multiples not of the atomic weight of hydrogen, but of $\frac{1}{2}$ the atomic weight of hydrogen - i.e., the hypothesis PCH ($\frac{1}{2}$; H=1).[45] This hypothesis, which was suggested again soon afterwards by Maumene,[46] was received unfavourably by the scientific community in general. It was reiterated in 1857 by Dumas,[47] who in the following year found it necessary to go a step further and suggest

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[40] The Bridgewater Treatises on the Power, Wisdom and Goodness of God as manifested in the creation: VIII - Chemistry, Meteorology and the Function of Digestion, William Prout, London, 1834; pp.137-8.

[41] The currently-accepted value for the C:H ratio was not integral.

[42] Dumas and Stas, Comptes rendus, 11 (1840) 287.

[43] Comptes rendus, 14 (1842) 537-47.

[44] J. prakt. Chem., 23 (1841) 159; 26 (1842) 461.

[45] Ann. der Chemie, 38 (1841) 92; Schweizer Gesell-Verh., 1843, 62-6.

[46] Ann. chim. phys., 18 (1846) 41.

[47] Compt. rend., 45 (1857) 709-31.

PCH ($\frac{1}{4}$; H=1),[48] a proposal which was criticised by Schneider on the grounds that it deprived Prout's hypothesis of all interest and value.[49]

In 1860 Stas published a series of experimental results which provided very strong evidence against PCH (1; O=8, or H=1),[50] and which for many chemists heralded the demise of this hypothesis. Stas himself claims to have begun his experiments with "an almost absolute confidence in the exactness of Prout's principle",[51] but that after the results he "reached the complete conviction ... that Prout's law, with all the modifications due to M. Dumas,[52] is nothing but an illusion, a pure hypothesis expressly contradicted by experiment."[53]

Marignac (1860), in a review of Stas' results, defended what he called "Prout's law", by which he clearly meant PCH ($\frac{1}{2}$; O=8):[54] "... if they [sc. Stas' values] do not coincide absolutely with the numbers of Prout,[55] they are so close to them that it is impossible to consider this fact as accidental. Thus for the nine determinations resulting from this work of

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[48] Ibid., 46 (1858) 951-3; 47 (1858) 1026-1034.

[49] Ann. der Phys. (Pogg), 107 (1859) 619. Schneider's criticism was rather too strong; PCH ($\frac{1}{4}$; H=1) is certainly less satisfactorily testable by experiment than are PCH (1; H=1) and PCH ($\frac{1}{2}$; H=1), but it is not, and was not at the time, utterly incapable of experimental test.

[50] Bulletin de l'Académie Royale de Belgique [2], 10 (1860) 208-336. Portions in English translation are given in Bibl.95. Stas expressed his "atomic weights" according to the standard $1 = \frac{1}{8}O$ (O =8, and not O = 16, being taken as the "atomic weight" of oxygen). He found the difference between the "atomic weights" of ammonium and nitrogen to be 4.02 instead of 4.00, and concluded that "the error exists rather in the atomic weight of hydrogen than in that of nitrogen" (Bibl.95, p.47) i.e., Stas thought that relative to O=8, H should perhaps be 1.005, and not exactly 1. The hypotheses to which his "atomic-weight" values were directly relevant were therefore PCH ($\frac{1}{n}$; O=8), and not PCH ($\frac{1}{n}$; H=1). But even assuming H = 1.005 (O=8), Stas' results are still found to disagree not only with PCH (1; O=8) but also with PCH (1; H=1).

[51] Bibl. 95, p.44.

[52] Dumas' modifications were PCH ($\frac{1}{2}$; H=1) and PCH ($\frac{1}{4}$; H=1).

[53] Bibl. 95, p.45.

[54] This is clear from a column of atomic-weight values given in his paper (see Bibl.95, p.51) which he labels "Prout", and which includes Cl = 35.5, Pb = 103.5. Marignac is sceptical of Stas' conclusion that the O = 1 ratio is not exactly 8:1 (see Bibl. 95, p.52), and seems to consider that PCH ($\frac{1}{2}$; O=8) is equivalent to PCH ($\frac{1}{2}$; H=1).

[55] These "numbers of Prout" being integral multiples of 0.5 (H=1, or O=8).

Stas, the difference is as a mean 0.056, say $\frac{1}{18}$ of the equivalent of hydrogen, or $\frac{1}{9}$ of the half-equivalent".[56] In the same paper Marignac gave what seems to be the earliest suggestion of the possibility of a breakdown of the law of conservation of weight for the formation of chemical atoms from protyle atoms, an ad hoc hypothesis which enables a simple PCH to be rejected without rejection also of the corresponding PPH:

> Could we not suppose that the cause (unknown but probably different from the physical and chemical agencies familiar to us) which has determined certain groupings of the atoms of the sole primordial matter so as to give rise to our chemical atoms, by impressing on each of these groups a special character and particular properties, should not at the same time have exercised an influence on the manner according to which these groups of primordial atoms would obey the law of universal attraction, in such wise that the weight of each group might not be exactly the sum of the weights of the primordial atoms composing it?[57]

One of the few scientists who showed an adherence to PCH (1; H=1) in the 1860's was the geologist and mineralogist de Chancourtois. In 1862 (in the paper in which he introduced his spiral classification of the elements - his "vis tellurique"[58]) de Chancourtois ventured the opinion that under certain special conditions which had yet to be realised or understood, the hypothesis PCH (1; H=1) holds strictly: "I think that ... in all determinations of constants which we wish to compare, they must be reduced to the same conditions. ... Prout's law ... presents itself as furnishing a means for reducing experimental observations to a comparable state by a

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[56] Bibl. 95, pp. 56-7.

[57] Bibl. 95, p.58. For a similar view by Mendeleev (1871) see Ch.I, and later in the present chapter. In 1900 George Rudorf (a pupil of Ramsay's) made the following related suggestion: "We know that the atoms attract one another in the molecule; and if the atom be a complex system of protyles, then we must conclude that the protyles also attract one another in the atom. The cohesive force between the protyles is very great compared with the action of gravity on them, and therefore it may, and probably does, affect the weight of a system of protyles. With molar masses the attractions are not perceptible, and we have therefore no right, in our ignorance of the nature of gravitation, to assume that the weight, as we measure it, of n protyles is n times that of one protyle ... No doubt the gravitation law will hold approximately, and hence the atomic weights must approximate to integral values, and this we find actually to be the case. The actual differences between experimental and integral values will in some measure depend on the structure of the atom. Probably, therefore, in the case of chlorine, the protyles are grouped together in some abnormal manner ..." (The Periodic Classification and the Problem of Chemical Evolution, London, 1900, p.170).

[58] Compt. rend., 54 (1862); an English translation is given by P.J. Hartog, Nature, 12 (1889) 186-8. De Chancourtois' "vis tellurique" is discussed in Ch.III of this thesis.

series of trials, without this state being even a completely defined one, but, on the contrary, in order to define it".[59]

The tendency to reject PCH ($\frac{1}{2}$; H=1) after Stas' results was, as might be expected, rather less than for PCH (1; H=1). In addition to Marignac various other chemists also retained a certain degree of belief in PCH ($\frac{1}{2}$; H=1). Odling, for example, wrote in 1863: "At the present time, out of the fifty-eight elementary atomic weights ... not more than half a dozen differ appreciably from multiples by whole numbers of half the atomic weight of hydrogen. Some of these exceptional numbers ought probably to be doubled, whereby they would accord with Prout's modified law,[60] while others can hardly be looked upon as satisfactorily determined".[61]

G.D. Hinrichs, in his publications of 1866 and 1867, employed the idea of a single primary substance whose atoms are of weight $\frac{1}{4}$H (1866) or $\frac{1}{2}$H (1867), expressing the atomic weight of the elements as exact integral multiples of these units.[62]

It was during the 1860's that Mendeleev's comments on Prout's hypothesis began to appear: these will be discussed in section C.

Attention was again drawn to Prout's hypothesis in its original form - i.e., to PCH (1; H=1) - at the end of the 1870's, by Dumas' demonstration (1878) of an error in the work of Stas, and by Mallet's revision (1880) of the atomic weight of aluminium, and the remarks he appended to the publication of his results. Dumas showed that occluded oxygen in the silver used by Stas had almost certainly caused a significant error in Stas' determination of the atomic weight of silver.[63] And since this atomic-

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[59] Hartog's translation (op.cit.), 186. It is clear from elsewhere in the same paper that by "Prout's law" de Chancourtois here means PCH (1; H=1).

[60] This is the only instance I have come across of the suggestion that a PCH may provide an indication of whether or not the correct multiple of the equivalent weight of an element is being used for the atomic weight.

[61] Bibl. 129, vol.I, 1863, 455-6.

[62] See Ch. III.

[63] Compt. rend., 86 (1878) 65. Marignac, in 1860 (see Bibl.95, p.56), had mentioned the possibility of error from this source, but did not feel it to be significant.

We have already come across two earlier contributions by Dumas in connection with Prout's hypothesis: his revision of atomic weights (C, O) around 1840, resulting in a revival of support for PCH (1; H=1) at this time; and his proposal of PCH ($\frac{1}{2}$; H=1) and PCH ($\frac{1}{4}$; H=1) in 1857-8. (Dumas lived from 1800 to 1884).

weight value was of central importance in Stas' work, the question again arose as to whether PCH (1; H=1) may in fact be true. Mallet's experiments had indicated an atomic weight of 27.0 for aluminium, which led him to remark, "this result ... adds one to the cases already on record of the numbers representing carefully determined atomic weights approaching closely to integers, and leads to a word on the reconsideration of 'Prout's law'."[64] Mallet goes on to say -

> ... the most careful work which has been done by Stas and others only proves by the close agreement of the results that fortuitous errors have been reduced within narrow limits. It does not prove that all sources of constant error have been avoided, and indeed this never can be absolutely proved, as we never can be sure that our knowledge of the substances we are dealing with is complete ...
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> ... we discard altogether Dumas' assumption of multiples of .5 or .25, and consider simply the indications afforded of Prout's law in its original form ... It appears that out of the 18 numbers,[65] 10 ... approximate to integers within a range of variation less than one-tenth of a unit. What then is the degree of probability that this is purely accidental, as those hold who carry to the extreme the conclusions of Berzelius and Stas? Since there are five intervals of .1 each between any integer and the .5 which divides it from the next higher (or lower) integer, the result is given by the expression
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> $$5^{-18}\left[1+\frac{\lfloor 18}{\lfloor 17}\times 4+\frac{\lfloor 18}{\lfloor 16\ \lfloor 2}\times 4^2+\frac{\lfloor 18}{\lfloor 15\lfloor 3}\times 4^3+\ldots\ \frac{\lfloor 18}{\lfloor 10\ \lfloor 8}\times 4^8\right]$$
>
> and the probability in question is found to be only equal to 1:1097.8.
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> ... this example ... seems sufficiently to illustrate the point that not only is Prout's law[66] not as yet absolutely overturned, but that a heavy and apparently increasing weight of probability in its favour, or in favour of some modification of it, exists and demands consideration.[67]

In 1881-2 A.M. Butlerov published certain remarks on atomic weights and Prout's hypothesis.[68] He acknowledged that "after the classic work of Stas we have to accept as a fact that the atomic weights are not expressed (in relation to hydrogen) by whole numbers, but at the same time they usually approximate to whole numbers to such an extent that this approximation

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[64] The revision of the atomic weight of aluminium, Phil. Trans. Roy. Soc., 171, Part III (1880) 1003-35; p.1033.

[65] Mallet appends a table of 18 atomic weights, based on H=1 (e.g., he gives O=15.961).

[66] Mallet is referring here to PCH (1; H=1).

[67] Op. cit., 1033-35.

[68] J. Russ. Phys.-Chem. Soc., 13 (1881) 175; 14 (1882) 208-12.

cannot be considered accidental, and it is difficult to admit that Prout's hypothesis was devoid of any real basis".[69] Butlerov felt that Prout's hypothesis may, "under certain conditions, be completely true",[70] advocating the idea of the variability (according to conditions) of the atomic weight of a given element,[71] and characterising the atomic weight as "nothing other than the expression of that quantity by weight of matter which is the bearer of a certain quantity of chemical energy".[72]

In 1882 F.W. Clarke wrote a paper entitled A recalculation of the atomic weights.[73] Taking O=16 as his standard, Clarke found most atomic weights to be almost exact multiples of $\frac{1}{2}$, and concluded that the few apparent exceptions arose from undetected constant errors. He comments, "I began this re-calculation ... with a strong prejudice against Prout's hypothesis, but the facts as they came before me have forced me to give it [sc. PCH ($\frac{1}{2}$; O=16)] a very respectful consideration."[74]

In the same year Lord Rayleigh had the following to say on the subject of Prout's hypothesis in his presidential address to the Mathematical and Physical Science Section of the British Association:

> I should like to make a remark or two ... on Prout's law, according to which the atomic weights of the elements, or at any rate of many of them, stand in simple relation to that of hydrogen. Some chemists have reprobated strongly the importation of a priori views into the consideration of the question, and maintain that the only numbers worthy of recognition are the immediate results of experiment.

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[69] 1882, p.210. In a footnote to this passage Butlerov refers to the comments of Marignac (1860) and Mallet (1880) on the unlikelihood that the observed close approximation of the atomic weights to the values demanded by Prout's hypothesis represents a "chance" result.

[70] 1882, p.211.

[71] In his 1882 paper Butlerov clearly seems to advocate variability of atomic weights in the sense that a given sample of an element may be able to change its atomic weight according to the physical conditions, not in the sense of the existence of different samples of a given element with different but constant atomic weights. It is for this reason that I cannot accept the claim, not infrequently made (e.g., by A.I. Brodskii in Khimiia Izotopov, Moscow, 1952, pp. 9-11), that in the sources under consideration Butlerov shows an anticipation of "isotopes".

[72] 1882, p.211. It is difficult to see how Butlerov visualises the mechanism by which a given sample of an element can change its atomic weight; perhaps he is not here concerned with mechanisms (although this would contrast rather sharply with his work on structural organic chemistry). Possibly, as W.V. Farrar has suggested (Bibl.20, p.318), Butlerov may here be thinking of weight in a sense similar to that proposed by Mendeleev in 1871, as some sort of compound effect of matter and "inner motion". However, although Butlerov in his 1882 paper does explicitly express his sympathy with Mendeleev's conjecture that weight may be a compound effect of matter-plus-motion, he nevertheless seems to distinguish Mendeleev's idea from his own ideas regarding the variability of atomic weights (see his 1882 paper, p.209).

[73] Smithsonian Institute, 1882.

[74] Op.cit., p.280. This comment provides an interesting contrast with Stas' remarks of 1860 quoted above.

> Others, more impressed by the argument that the close approximations to simple numbers cannot be merely fortuitous, and more alive to the inevitable imperfections of our measurements, consider that the experimental evidence against the simple numbers is of a very slender character, balanced, if not outweighed, by the *a priori* argument in favour of simplicity. The subject is eminently one for further experiment; and as it is now engaging the attention of chemists, we may look forward to the settlement of the question by the present generation. The time has perhaps come when a redetermination of the densities of the principal gases may be desirable - an undertaking for which I have made some preparations.[75]

The series of experiments by Rayleigh on the densities of gases which followed the "preparations" to which he here refers did not support PCH (1; H=1). They did however lead directly to the discovery of the inert gases in the 1890's.[76]

In 1884 J.A.R. Newlands referred to "Prout's law", acknowledging that "though it is not true that all the atomic weights are multiples of the atomic weight of hydrogen, it is nevertheless the case that the number of elements whose atomic weights approach within experimental errors to exact multiples of hydrogen is far greater than it should be on the theory of probabilities".[77]

A very important figure in the history of Prout's hypothesis and related fields during the late 19th century was William Crookes. In his address to the British Association in 1886 Crookes said:

> But if the evidence in favour of Prout's hypothesis in its original guise is deemed insufficient, may not Mr. Clarke's suggestion of half multiples place it upon an entirely new basis? Suppose that the unit of the scale ... is not hydrogen but some element of still lower weight? We are here at once reminded of helium, - an element purely hypothetical as far as our earth is concerned, but supposed... to exist in the sun and other stellar bodies.[78]

Later in this same address, after introducing the idea of a single

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[75] Chem. News, 46 (1882) 96-7. Reprinted in Bibl.47, pp. 373-4.

[76] The history of the discovery of the inert gases is outlined briefly in Ch. VII.

[77] Bibl.84, pp.32-3. Newlands undoubtedly here has Mallet's work (1880) in mind.

In the paragraph preceding the one quoted here Newlands (ibid., p.32) touches upon the question of the structure of the elements: "If we view all matter as really composed of various modifications of one elementary substance, consisting of physical atoms, we may regard the atomic weight of each element as expressing the relative number of physical atoms contained in the chemical atom. The same number of physical atoms differently arranged might form two or more distinct elements which might then be regarded as isomeric. Perhaps cobalt and nickel are thus related".

[78] Chem. News, 54 (1886) 117-8.

"protyle" out of which all of the chemical elements have been formed by "some process akin to cooling",[79] Crookes remarked:

> I have said that the original protyle contained within itself the potentiality of all possible atomic weights. It may well be questioned whether there is an absolute uniformity in the mass of every ultimate atom of the same chemical element. Probably our atomic weights merely represent a mean value around which the actual atomic weights of the atoms vary within certain narrow limits.
>
> ... I conceive ... that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that while the majority of the calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 and 42, and so on.[80]

Insofar as Crookes is here suggesting the existence of different varieties of atom, with different (but constant) atomic weights, for a given element, then (unlike Butlerov - see above) his remarks can justifiably be considered as anticipating the idea of "isotopes". However we should not read too much into Crookes' characterisation here of these "isotopes" as possessing exactly integral atomic weights,[81] because in the following year he wrote -

> When ... we say that, e.g., the atomic weight of calcium is 40, the actual fact may well be that whilst the majority of the calcium atoms really have the atomic weight of 40, some are represented by 39.9 or 40.1, a smaller number by 39.8 or 40.2, and so on. The properties which we perceive in any element are thus the mean of a number of atoms differing among themselves very slightly, but still not identical.[82]

By about 1890 a controversy had developed over whether atomic weights should be expressed according to the standard H=1 or $\frac{1}{16}$ O=1. This arose out of the uncertainty of the value of the O:H ratio, and the fact that most experimental determinations of atomic weights actually measured the weights relative to oxygen. Because of this latter fact each revision

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[79] Ibid., p.122. Crookes' "protyle" is a non-atomic primordial matter out of which the (non-composite) chemical atoms have condensed. Crookes' use of the term "protyle" is therefore rather different from the sense in which it is used by certain other scientists of the late 19th century and early 20th century (e.g., Rudorf - see n.57 above), and in which it is used in this thesis in the expression "Proutian protyle hypothesis", where "protyle" is the atomic primary matter which, by different degrees of aggregation of its atoms, gives the various chemical atoms.

[80] Ibid.

[81] Such as, for example, seeing in this passage an attempt by Crookes to save PCH (1; H=1) in the sense that all "isotopes" obey this hypothesis strictly, even though the mixing of the "isotopes" of a given element masks this fact in ordinary experimental determinations of the atomic weight.

[82] Chem. News, 55 (1887) 97.

of the O:H ratio meant that, for the traditional atomic-weight system based upon H=1, the atomic weight not only of oxygen but also of many other elements had to be changed. This unsatisfactory state of affairs led, by the mid-1890's, to the general adoption of $\frac{1}{16}$ O=1 as the unit of the atomic weights.[83]

With the adoption of the atomic-weight standard O=16 the values of the atomic weights exhibited an appreciably greater tendency to approximate to whole numbers than they had on the standard H=1. This difference was clearly brought out in certain calculations, made in the early 20th century, of the probability of the atomic weights' approaching as closely as they do to whole numbers merely by chance. Of particular interest in this respect is a paper on The ratios of the atomic weights by A. Marshall (1902).[84] Marshall refers to a calculation by M. Rudolph (1901) which had arrived at a probability of 135 : 1 against the atomic weights (referred to H=1) of a particular set of 18 elements approaching integers as closely as they do by chance,[85] and reports that when he repeated Rudolph's calculation for the same weights referred to O=16 he found a probability of 4120 : 1 against. As Marshall himself concluded, "When these atomic weights are referred to O=16 their tendency to approach whole numbers is therefore about thirty times as great as when they are referred to H=1".[86] Another probabilistic assessment of PCH (1; O=16) was made by R.J. Strutt (1901), who arrived at the following conclusion:

> It appears, then, that a calculation of the probabilities involved fully confirms the verdict of commonsense, that the atomic weights tend to approximate to whole numbers far more closely than can reasonably be accounted for by any accidental coincidence. The chance of any such coincidence being the explanation is not more than 1 in 1000,[87] so that ... we have stronger reasons for believing in the truth of some modification of Prout's law, than in that of many historical events which are universally accepted as unquestionable.[88]

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[83] This adoption of the atomic-weight standard $\frac{1}{16}$ O=1 instead of H=1 is discussed by Venable, Bibl. 124, p.233. It is clearly reflected in Mendeleev's work of the 1890's, e.g., see PLBA, 411-12 (1892), 244 (1898). In his article on the nature of the ether published in 1903 (1905) Mendeleev suggested that an advantage of the rejection of H=1 as atomic-weight standard was that it tended to encourage the expectation of new chemical elements lighter than hydrogen (PLBA, 489, footnote).

[84] Chem. News, 76 (1902) 88-89; from Chemiker Zeitung, July 19, 1902.

[85] Rudolph, Chem. Zeitung, 25 (1901) 1134.

[86] Op. cit., p. 88.

[87] The calculation of this figure, which was made for a set of 8 elements (atomic weights referred to O=16) using a formula given by Laplace, is to be found earlier in Strutt's paper (pp.312-13).

[88] Phil. Mag., 1 (1901) 311-14; pp. 313-14.

Neither Strutt nor Marshall attempted to interpret his results in terms of any "protyle" hypothesis.

In addition to the empirical grounds provided for conjectures about primary matter and the complexity of the elements by the evidence supporting Proutian-type hypotheses of a simple commensurability of atomic weights, numerical relationships of another sort between atomic weights also provided grounds upon which were based certain ideas of the complexity of the elements: these were the relationships between the atomic weights of chemically-similar elements. This latter subject overlaps to a large extent with that of analogy of the elements with organic radicals and compounds (see later); but there is one type of numerical relationship between the atomic weights of chemically-similar elements which was taken as evidence of the complexity of a chemical element at a time when the homologous series of organic chemistry had yet to be recognised.[89] This is the so-called "triad-relationship", where the middle element (according to its atomic-weight value) of a group of three chemically-similar elements has an atomic weight equal to the arithmetic mean of the other two elements of the "triad". The triad-relationship was discovered in 1816-17 by J.W. Döbereiner, and led him to suggest that strontium is some sort of mixture or combination of calcium and barium.[90] In the early 1850's the triad-relationship was again taken as an indication that the middle element of a triad may be composed of the two extreme elements, e.g., by Dumas in 1851.[91] But in the course of this decade the "triad-argument" for complexity came to be entirely superseded by arguments based upon analogy between the atomic-weight relationships within groups of three or more chemically-similar elements (and sometimes even dissimilar elements), and the homologous and polymeric relationships of organic chemistry.

b) Decomposition, synthesis and transmutation of the elements as evidence of their complexity or of the existence of some underlying primary matter (or few types of primary matter).

Most chemists of the period under consideration acknowledged that the

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[89] Organic homologous series were recognised early in the 1840's, first probably by J. Schiel in 1842. The term "homologous" originated with Gerhardt, in 1845.

[90] The first publication presenting Döbereiner's discovery of the triad-relationship was by Wurzer, Ann. der Phys. (Gilbert), 56 (1817) 332. The first paper on the subject by Döbereiner himself was in the same journal, 56 (1817) 435. A second (and final) article by Döbereiner on triads was given in Ann. der Phys. (Pogg.), 15 (1829) 301.

[91] Athenaeum, 1851, 750 (given in Bibl.47, p. 352); Amer. J. Sci. [2], 12 (1851) 275.

strongest kind of evidence for the complexity of the substances classed as chemical elements, or for the existence of a single primary substance (or small number of primary substances) underlying these elements, would be some sort of well-authenticated decomposition, synthesis or transmutation of the elements. As would be expected, however, there was much difference of opinion in connection with the various claims of decomposition, synthesis and transmutation which were actually made: there were disagreements about the authenticity and reliability of particular experimental results, and about the interpretation and theoretical significance of particular empirical data. In addition to these disagreements over what we may call "positive" evidence, there were also (mainly before the late 1890's [92]) differences of opinion regarding the significance for the question of the nature of the chemical elements of the "negative" data, i.e., of the observed immutability of the elements under a wide variety of conditions, and the failure of attempts to produce decomposition, synthesis or transmutation experimentally. On the one hand there were those who considered that such negative data provided strong evidence against hypotheses of primary matter and the complexity of the elements, e.g., Berzelius (1844),[93] Despretz (1859);[94] and on the other there were those who, advocating some theory of primary matter or complexity, claimed that the elements had so far remained immutable only because the techniques required to synthesise or change them had yet to be discovered, e.g., Faraday (1818),[95] Dumas (1859)[96] and Gladstone (1883).[97]

Some of the more notable claims of empirical evidence of decomposition, synthesis or transmutation of chemical elements for the period from ca. 1840 to ca. 1905 are considered below.

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[92] Before the discovery of the electron and of radioactivity.

[93] Amer. J. Sci. (Silliman), 48 (1845) 369-72 (translation of a letter from Berzelius, dated 6 Dec., 1844).

[94] Compt. rend., 48 (1859) 462. (See Venable, Bibl. 124, pp. 49-50).

[95] See H. Bence Jones, The Life and Letters of Faraday, 2nd edn., vol. I (1870).

[96] Ann. Chim. Phys. [3], 55 (1859) 129.

[97] Nature, 28 (1883) 500-3.

In the early 1840's Samuel Brown (of Edinburgh) - who believed in the possibility of transmutation of the elements by synthesis but not by decomposition[98] - carried out certain experiments in which he claimed to have synthesised silicon from the carbon contained in paracyanogen, and to have converted iron into rhodium.[99] In 1841 G. Wilson and J.C. Brown repeated Samuel Brown's experiments on paracyanogen,[100] and in some cases (but not all) did indeed obtain a product which they acknowledged as being silicon, in quantities which, although much smaller than had been claimed by S. Brown, were larger than Wilson considered likely to have been due to "an impurity or accidental ingredient".[101] However, although Wilson was prepared to conclude that S. Brown's experimental results were "authentic",[102] he did not accept that they provided proof of the transmutation of carbon into silicon: "They are too imperfect to establish the truth of that proposition in the hands of any one; ... there exists at present no evidence, in the way of demonstration by experiment, to satisfy a chemist, that carbon or any other element has ever suffered transmutation".[103] Most other chemists totally dismissed S. Brown's results.[104]

During the period 1873-87 J.N. Lockyer presented the view - based upon a consideration of certain spectral data obtained by himself and by others -

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[98] Brown's belief in the possibility of transmutation of the elements by synthesis but not by decomposition provides an interesting contrast with a view expressed by Mendeleev in 1897 (PLBA, 448-9; see later).

[99] Trans. Roy. Soc. Edinburgh, 15 (1841) 165-76, and 229-46. (Paracyanogen is a polymer of cyanogen).

[100] Ibid., pp. 547-559.

[101] G. Wilson, The Edinburgh New Philosophical Journal, 37, no. 73 (July 1844) 1-21; p.16.

[102] Ibid., p.17.

[103] Ibid.

[104] Liebig, for example, wrote (Familiar Letters on Chemistry, 1843, London, 1st ed., p.55), "Mr. Brown of Edinburgh thought he had converted iron into rhodium, and carbon or paracyanogen into silicon... But his experiments have been carefully repeated by qualified persons, and they have completely proved his ignorance; his rhodium is iron, and his silicon an impure incombustible coal". (See Bibl.47, p.144).

One chemist who did not dismiss S. Brown's results was G.J. Knox (Chem. Gazette, Sept. 1843). However, Knox did not agree with S. Brown's interpretation of these results, but suggested instead that the silicon was produced by decomposition of the nitrogen in paracyanogen; according to Knox, nitrogen comprises silicon and hydrogen, and perhaps also oxygen.

that under extreme conditions such as exist in the sun there occurs a dissociation of chemical elements.[105] For example, he observed that the emission spectrum of iron given by the solar protuberances lacked sometimes one part of the usual iron spectrum, and sometimes another part; and that the Fraunhofer spectrum of iron sometimes showed one part of the spectrum shifted in relation to the other part. From these data Lockyer concluded that iron is dissociated into two or more components at the temperature of the sun.

Lockyer's views on the dissociation of the chemical elements seem generally to have been received unfavourably; he was even dubbed an alchemist by some of the chemists who heard his paper to the Royal Society in December 1878.[106] In the 1880's Lockyer's conclusions were criticised by Mendeleev, on the basis of contributions by Zöllner and by Kleiber (see later). However, one scientist who reacted favourably to Lockyer's claims was William Crookes, who said (1886): "Mr. Lockyer has shown, I think on good evidence, that, in the heavenly bodies of the highest temperature, a large number of our reputed elements are dissociated, or, as it would perhaps be better to say, have never been formed".[107]

In 1897 it was shown (independently) by Wiechert,[108] J.J. Thomson[109] and Kaufmann[110] that cathode rays[111] consist of small material particles

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[105] See especially Lockyer's paper Discussion of the working hypothesis that the so-called elements are compound bodies, Nature, 19 (1879) 197-201, 225-230; and his Chemistry of the Sun, London, 1887. An account of "Lockyer's hypothesis of the dissociation of the elements" is given by McGucken in Bibl.64, pp.83-101. W.H. Brock has published a paper on Lockyer and the Chemists : the first dissociation hypothesis, Ambix, 16, July 1969 (nos. 1 and 2), 81-99.

It should perhaps be stressed that we are here considering Lockyer's claims, on the basis of spectral data, of a dissociation of the elements, not merely of their complexity. The question of spectral evidence for the complexity of the elements over and above the evidence which was taken to indicate their dissociation is considered later.

[106] See Brock, Ambix, 1969, p.92.

[107] British Association Reports, 55 (1886) 559.

[108] Ann. Phys., 61 (1897) 544.

[109] Electrician, 39 (21 May, 1897) 104-8; Proc. Roy. Inst., 15 (1897) 419-32; Phil. Mag. [5], 44 (1897) 293.

[110] Ann. Phys., 62 (1897) 588.

[111] Cathode rays were discovered by Julius Plücker, 1859.

with a negative electrical charge. Wiechert called these particles "electrons",[112] and Thomson called them "corpuscles". Commenting on the behaviour of cathode rays in electric and magnetic fields, Thomson wrote: "The explanation which seems to me to account in the most simple and straightforward manner for the facts is founded on the view of the constitution of the chemical elements which has been favourably entertained by many chemists; this view is that the atoms of the different chemical elements are different aggregations of atoms of the same kind".[113] Thomson cited as support for his view the "weighty arguments, founded on spectroscopic considerations, in favour of the composite nature of the elements"[114] which had been proposed by Lockyer.

The various observations of the late 1890's and early 20th century that the cathode-ray "corpuscles" appeared to be the same for different gases and for different kinds of electrode in the discharge tube, and that these corpuscles could be produced by other means also, e.g., by heating metals to incandescence, by the action of ultraviolet radiation or X-rays upon metals, and spontaneously by radioactive substances, strengthened the idea of the electronic constitution of the chemical atom.[115]

As a result of experiments on the radioactivity of thorium and its "emanation", Rutherford and Soddy (1902) concluded that radioactivity is a manifestation of the spontaneous disintegration of chemical atoms, resulting in the production of one element from another.[116] In 1903 Ramsay and Soddy demonstrated that helium is produced by a solution of radium bromide in water, and by radium "emanation".[117] A year later, Boltwood, McCoy and R.J. Strutt showed, independently, that radium is produced by spontaneous transmutation of uranium.[118] In 1905 Boltwood claimed, on the basis of the

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[112] The term "electron" had been proposed in 1891 by G.J. Stoney, for the unit charge on the hydrogen ion (earlier he had used the term "electrine").

[113] Phil. Mag. [5], 45 (1897) 311.

[114] Proc. Roy. Inst., 15 (1897) 432.

[115] See, for example, J.J. Thomson's article On the structure of the atom, Phil. Mag. [6], 7 (1904) 237.

[116] J. Chem. Soc., 81 (1902) 837-60; Phil.Mag. [6], 5 (1903) 576-91.

[117] Chem. News, 88 (1903) 100-101.

[118] See Bibl. 130, p.784.

lead content of uranium ores, that lead is the final product of the radio-active disintegration of uranium.[119]

c) Views based upon analogy of the elements with compound radicals and organic compounds.

During the period under consideration a large number of chemists argued in favour of the complexity of the elements on the basis of various types of analogy of the latter with the compound radicals (both inorganic and organic) and organic compounds. Over and above the "general" analogy which was commonly recognised between the chemical elements and the compound radicals, that they both "persist" in some sense through chemical changes (albeit all changes in the case of elements, but only a certain class of changes for the radicals), various "specific" analogies were also drawn, some of which involved analogy of the elements with not only compound radicals but also organic compounds. These "specific" analogies may be classified into two types -

i) those between the properties of certain elements on the one hand, and of particular inorganic radicals on the other, e.g., between the alkali-metal elements and the ammonium radical, or between the halogens and the cyanide radical;

and

ii) those between the relationships within a group of chemical elements on the one hand, and within a series of organic radicals or compounds on the other.

An early example of type i) was provided by Davy in 1812, when on the basis of the existence of ammonium amalgam he suggested that the metals, like ammonium, are complex substances containing hydrogen.[120] A later chemist who used the analogy between certain elements and NH_4 and CN as an argument for the complexity of the elements was Pettenkofer (1850);[121] Mendeleev, also, thought that this analogy provided some indication of the complexity of the elements (see later).

Specific analogies of type ii) began to be drawn in the mid-19th century, and from this time onward were frequently used as one of the bases upon which arguments for the complexity of the elements were founded. From the early 1850's there was a rapid growth in the search for atomic-weight

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[119] Amer. J. Sci., 20 (1905) 239, 253.

[120] Elements of Chemical Philosophy, 1812, p. 275.

[121] Gelehrte Anzeigen der Akademie der Wissenschaften zu München, 30 (1850) 261.

relationships within groups of (usually chemically-similar) elements.[122] The various relationships which were discovered were often compared to the homologous relationships within series of organic radicals and compounds and sometimes to the polymeric relationships within series of organic compounds, such analogies being taken by the majority of chemists (including Mendeleev - see later) to indicate complexity of the elements. A notable development in this field occurred in the early 1880's when Pelopidas (1883)[123] and Carnelley (1886)[124] drew analogies between the periodicity of the elements on the one hand and certain periodic relationships among the organic radicals on the other. Carnelley concluded that "the elements as a whole are analogous to the hydrocarbon radicles".[125] and went on to propose the following tentative hypothesis: "... whereas the hydrocarbons are compounds of carbon and hydrogen, the chemical elements [sc. apart from hydrogen] would be compounds of carbon with ether (atomic-weight = -2) the two sets of bodies being generated in an exactly analogous manner from their respective elements. There would hence be three primitive elements, viz., carbon, hydrogen, and ether".[126]

d) The periodicity of properties of the elements as evidence for primary matter and the complexity of the elements.

Whereas Pelopidas and Carnelley took analogy between the periodicity of properties of the elements and certain periodic relationships among the organic radicals as evidence for the complexity of the elements, there were a great many scientists who without consideration of any such analogy took the periodicity of the elements as strong evidence in itself for their complexity or for the existence of a smaller number of primary substances.

Of those who were directly involved in the discovery of the periodic law (see Ch.III) only Mendeleev and Lothar Meyer seem to have considered the relevance of this law for the question of the nature of the elements. Mendeleev's views are considered later. Lothar Meyer's belief that the

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[122] See Ch. III.

[123] J.Russ. Phys.-Chem. Soc., Chem. Section, 15 (1883), no. 5, 364-6 (R).

[124] Chem. News, 53 (1886) 157-9, 169-72, 183-6, 197-200. (Given in Bibl. 47, pp. 390-404).

[125] Chem. News, 53 (1886) 169, 197.

[126] Ibid.,p.200. Carnelley's suggestion of a primitive element of negative atomic weight (the ether, at. wt.= -2) was made solely in connection with his speculations on the nature of the elements in the light of the analogy which he drew between their periodicity and certain periodic relationships among the organic radicals.

chemical elements are not ultimate entities appears to have been strengthened by the discovery of the periodicity of their properties.[127]

In 1887 W. Crookes remarked that the periodic law seems "to presuppose the existence of a genetic relation among the elements".[128] Henry Armstrong (1902) wrote:

> Although no direct evidence acceptable to chemists has been adduced which in any way justifies the belief that the elements are decomposable, it is impossible to resist the conclusion that they are genetically related... The generalisation known as the Periodic Law is in itself a justification of this view; the manner in which interrelationship becomes manifest when they are classified in accordance with its canons, being probably the strongest of all the arguments which can be cited as tending to show that the elements are compounds - but compounds very different from those with which we are accustomed to deal.[129]

Others holding similar views on this matter included Baumhauer (1870),[130] Savchenkov (1873),[131] Ostwald (1885),[132] Venable (1896)[133] and Beketov (1902).[134] Berthelot, while rejecting the periodic law, claimed (1885) that, "At bottom, those who invoke... the periodic series, bind everything to the conception of certain atoms smaller than those of the reputedly simple bodies".[135]

e) Views based upon spectroscopic data.[136]

During the period from the late 1860's to the mid-1870's line-spectra were commonly explained as being produced by molecules containing more than one chemical atom. But in 1875 an important experimental result was

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[127] See, for example, Die modernen Theorien der Chemie, 5th edn., 1884, pp. 129, 134.

[128] Chem. News, 55 (1887) 83.

[129] Chem. News, 86 (1902) 86.

[130] H. Baumhauer, Die Beziehungen zwischen den Atomgewichte und der Natur der chemischen Elemente, Brunswick, 1870.

[131] See PLSM, 451.

[132] W. Ostwald, Lehrbuch der Allgemeinen Chemie, 1885, p.127.

[133] Bibl. 124, pp. 9 and 10.

[134] O znachenii periodicheskoi sistemy D.I. Mendeleeva, Nauchnoe obozmie, No. 2 (Feb. 1902) 17-25.

[135] Given in Venable, Bibl.124, p.113 (translation from Berthelot's Les Origines de l'Alchimie, 1885, p.313).

[136] See McGucken, Bibl. 64.

published, viz., the value of the specific-heat ratio of mercury vapour (=1.66),[137] which strongly corroborated the indications of vapour-density measurements that the mercury molecule is monoatomic; and since mercury vapour gives a line-spectrum many scientists consequently came to believe in some sort of structure for the chemical atom. This attitude is exemplified in a comment of 1877 by Robert Bosanquet[138]:

> If we ask, why must we suppose the two atoms [sc. in a diatomic molecule] joined by elastic forces and not rigidly? We are told that it is the vibrations of the atoms that do the work we see in the spectroscope lines. But these lines occur in the vapour of mercury, for which our explanation fails to suggest any collocation of atoms more than one in the molecule. Why not, then, admit that the lines are produced by something within the atom which we cannot at present account for...?[139]

Many scientists at the time - especially in Britain - viewed this "something within the atom" as vibrations of a vortex atom.[140] Others who considered line-spectra to indicate a structure for the chemical atom but who did not invoke the idea of vortices (usually chemists rather than physicists) tended not to make any suggestion about the particular nature of the atoms, although there were a few who did propose specific hypotheses. Ciamician, for example, on the basis of spectral data which turned out later to be highly inaccurate, suggested in 1880 that the elements of the periodic table are compounded of the first element of the group with different amounts of oxygen[141]; and Grünwald, in 1887-8, also from very inaccurate spectral data, claimed that the chemical elements are compounds of two primary elements which he designated "a" and "b"[142].

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[137] Kundt and Warburg, Ueber die specifische Wärme des Quecksilbergases, Berichte der d. chem. Ges., 8 (1875) 945; and Ann. der Phys., 157 (1876) 353-69.

[138] Bosanquet was a lecturer in mathematics at Oxford.

[139] The velocity of sound, and ratio of specific heats, in air, Phil. Mag., 3 (1877) 276.

[140] See Ch.I, n.84.

[141] G.L. Ciamician, Spectroskopische Untersuchungen, Sitzungberichte der Matematisch-Naturwissenschaftlichen Classe der kaiserlichen Akademie der Wissenschaften, Wien, 82 (1880), Abt. 2, pp. 425-7. Also in 1880 Ciamician outlined his views on the nature of the elements, based upon his observations on "homologous spectra", in two letters to Mendeleev (see later).

[142] A.K. Grünwald, Astronomische Nachrichten, 117 (1887) 201-214; Chem. News, 56 (1887) 186-8, 201-2, 223-4, 232; Phil. Mag., 25 (1888) 343-50.

It is not clear whether Lockyer at any time regarded line-spectra as indicating a complexity of the chemical atoms independently of the indications which he cited as evidence of dissociation of the atoms, although W.N. Hartley certainly attributed such a view to him. Hartley understood Lockyer to have claimed that every element is composed of as many constituent parts as there are lines in its line-spectrum, and criticised this, saying, "with even very moderate dispersive power something like 1,200 lines can be recognised in the spectrum of iron, an element which has an atomic weight of 56, and it is simply inconceivable that a body of the chemical nature of iron can have a molecular structure so complex as to be composed of 1,200 simpler substances"[143] Hartley continued, "If ... we are to draw inferences as to the compound nature of substances from coincident lines in their spectra, it is not single lines but harmonic series that we must look to for coincidences".[144]

In 1896 Zeeman discovered the magnetic splitting of spectral lines (the "Zeeman effect").[145] The parallels observed in the Zeeman effect for different elements led Preston (1899) to the conclusion that "... these observations lend some support to the idea, so long entertained merely as a speculation, that all the various kinds of matter, all the various so-called chemical elements, may be built up in some way of the same fundamental substance".[146]

f) Views based upon other, miscellaneous, empirical grounds.

Some scientists of the 19th century considered the phenomenon of allotropy[147] to indicate a unity of matter. Berthelot, for example, wrote in 1885:

> ... carbon ... manifests itself in the free state in the most diverse forms and ... gives rise to many series of compounds corresponding in a certain manner with each of these fundamental forms,[148] as the compounds of an ordinary element correspond with that element ...
>
> ... carbon viewed in its different states and degrees of condensation is equivalent in itself to an entire class of simple bodies. O, S, Se, and Te by the same reasoning could represent the different states of a common element. Further, ozone, a body of very simple properties, and comparable therefore to a true element, has been really formed of oxygen, its existence to a certain extent

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[143] On homologous spectra, J. Chem. Soc., 43 (1883) 343-50.

[144] Ibid.

[145] Published 1897: Phil. Mag., 43 (1897) 226-39.

[146] Nature, 60 (1899) 178.

[147] The term "allotropy" was introduced in 1840, by Berzelius.

[148] Berthelot probably has in mind here the graphitic compounds discovered by Sir B.C. Brodie in 1859-60.

justifying the preceding conjecture [sc. of a single element common to O, S, Se and Te].[149]

A later view which also took the phenomenon of allotropy as grounds for belief in a single primary matter was that of Joachim Sperber (1896).[150] Such views as these seem to have arisen out of a failure to distinguish clearly between the concepts of "simple substance" and "element".

Other empirical grounds which were used in support of hypotheses of a single primary matter of the complexity of the elements included the action of gravity (Graham, 1863[151]), specific-heat measurements (Kopp, 1863[152]), and the distribution of the elements in the earth's crust (Crookes, 1886-7[153]). Graham, for example, argued that, "It is conceivable that the various kinds of matter now recognised as different elementary substances may possess one and the same ultimate or atomic molecules existing in different conditions of movement. The essential unity of matter is an hypothesis in harmony with the equal action of gravity upon all bodies".[154]

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[149] Given in Venable, Bibl. 124, pp.113-4 (translation from Berthelot's Les Origines de l'Alchimie, 1885, pp. 313-4).

[150] Das Parallelogram der Kräfte als Grundlage des Periodisches Systems in der Chemie, Zurich, 1896; reviewed in Chem. News, 74 (1896) 11.

[151] Speculative ideas respecting the constitution of matter (1863), an appendix to a paper On the molecular mobility of gases, Proc. Roy. Soc., 12 (1862-3) 620.

[152] Chem. News, 8 (1863) 90-91.

[153] Chem. News, 54 (1896) 122; 55 (1887) 97.

[154] Op. cit.

C. Mendeleev's views on the questions of primary matter and the complexity of the elements.[155]

The picture that tends to emerge from a study of the relevant primary and secondary sources available in English is that Mendeleev was utterly opposed to the ideas of a single primary matter and the complexity of the elements - that he unreservedly considered the elements to be immutable, qualitatively-distinct, ultimate forms of matter.[156] This is very much a misrepresentation of Mendeleev's actual views. That the English-language primary sources tend to present such a picture is merely an unfortunate consequence of the restricted amount of primary material available in English; that the misrepresentation has been perpetuated by English-language commentators with a knowledge of Russian, like Vucinich and Leicester, is less understandable, but is perhaps explained to some extent by an apparent failure on the part of these historians to distinguish two aspects of Mendeleev's attitude towards the ideas of primary matter and the complexity of the elements - on the one hand his attitude towards the question of the objective truth of these ideas (i.e. towards the question of their correspondence with reality), and on the other hand his attitude towards the relevance of these ideas to chemistry (and to science in general).

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[155] See Makarenia, Bibl. 60: D.I. Mendeleev on radioactivity and the complexity of the elements (R).

[156] Relevant primary sources available in English are:

i) The periodic law of the chemical elements, Chem. News, 40 (1879) 231-2, 243-4, 255-6, 267-8, 279-80, 291-2, 303-4; 41 (1880) 2-3, 27-8, 39-40, 49-50, 61-2, 71-2, 83-4, 93-4, 106-8, 113-14, 125-6. Reprinted in Bibl. 47, pp. 273-309. This paper was a translation of La loi périodique des éléments chimiques, Monitour Scientifique, 21 (1879, July) 691-737, which apart from a short foreword was itself a translation of Die Periodische Gesetzmässigkeit der chemischen Elemente, Annalen (Liebig), Suppl.VIII (1871), no. 2, pp. 133-229; this German paper had been translated (by F.R. Wreden) from Mendeleev's original Russian manuscript.

ii) Bibl. 66 (Pr. Ch., E-1, E-2 and E-3).

iii) Faraday Lecture, 1889: The periodic Law of the chemical elements. J. Chem. Soc., 55 (1889) 634-656; and as Appendix II in Pr. Ch., E-1, E-2 and E-3.

iv) An attempt towards a chemical conception of the ether, booklet, Longmans, London, 1904; and as Appendix III in Pr. Ch., E-3.

English-language secondary sources include:

i) Leicester, Bibl. 55.

ii) F.A. Paneth, Chemical Elements and Primordial Matter: Mendeleeff's view and the present position, in Bibl. 90, pp. 53-72.

iii) Alexander Vucinich, Bibl. 126.

The factors which for Mendeleev had some significance for the questions of primary matter and the complexity of the elements were the "philosophical" demand for unity and simplicity in nature, and the following "empirical" factors - the eventuality of a decomposition, synthesis or transmutation of the elements; the testable Proutian-type commensurability hypotheses; analogy of the elements with compound radicals and organic compounds; and the periodic law. Unlike the majority of his contemporary chemists and physicists Mendeleev did not consider spectroscopic data to be significant for the question of the nature of the elements.[157]

Mendeleev felt that the only kind of evidence which could conclusively establish ("prove") the complexity of the chemical elements, or the existence of some more fundamental form (or few forms) of matter, would be a well-authenticated empirical demonstration of a decomposition, synthesis or transmutation of the elements. But he never accepted any of the demonstrations which were claimed in this direction; and consequently throughout his career he regarded the hypotheses of a single primary matter and the complexity of the elements as lacking empirical proof. At the same time Mendeleev also explicitly acknowledged that these ideas had on the other hand not been refuted - they "can neither be denied nor accepted for want of sufficient data".[159] But despite the insufficiency of data (in Mendeleev's opinion) for deciding the question of the objective truth of the ideas of a single primary matter and the complexity of the elements, he seems to have been consistently inclined to believe that not only is it possible that the elements are complex entities, but it is even probable: in 1864, for example, he had said that "it is likely that all our simple bodies are not simple",[160] and in 1897 he write that he was "not opposed to, but rather inclined to accept, the idea of the complexity of the elements".[161] Towards the related, but not identical, idea of the existence of a single primary matter Mendeleev appears to have been less sympathetic, especially later in his career.

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[157] The details of Mendeleev's views on the significance or otherwise for the ideas of primary matter and the complexity of the elements of the various kinds of "empirical" ground listed in section A, including spectroscopic data, are presented later in the present section.

[158] In connection with the considerations of the present section Mendeleev's scientific career can be taken to cover the period 1860-1906.

[159] Pr. Ch., R-1 (1871): Colls., 14, 246. Pr. Ch., R-8 (1906) n. 636.

[160] Bibl. 75, p.16.

[161] PLBA, 448.

The factors which encouraged Mendeleev's belief in the objective truth of the idea of the complexity of the elements were of three kinds: the analogies of the elements with compound radicals and organic compounds; the periodic law; and the "philosophical" demand for a "unity of plan"[162] in the universe. The influence of this last factor - the "philosophical" ground - is seen in an argument presented by Mendeleev in 1871:

> ... the assumption that the atoms of the simple bodies are complex entities formed by the combination of certain still smaller parts (ultimates)... takes its basis from a comparison with the form of the universe. A molecule is compared to a solar system, a radical or an entire annexed (prisoedinisiaiushchaiasia) molecule to a planet and its satellites, the sun to a polyatomic [sc. polyvalent] element linking a whole aggregate of bodies, an atom to a separate heavenly luminary, satellite, planet, sun. But the composition of these luminaries, judging from all that we know, is the same. The type of matter is the same for all, i.e. these individuals are yet divisible by a multitude of means. So also for atoms.[163]

This is an argument in support of the view that the different kinds of chemical atom are all composed of the same ultimate substances: it is not an argument for the existence of a single primary matter. The idea of a single primary matter has its own "philosophical" ground, of course, corresponding as it does directly to a demand for unity; and this seems to have provided it with some aesthetic attraction for Mendeleev.[164] But counteracting this was Mendeleev's view, certainly later in his life, that the periodic law tends to refute the idea of a single primary matter (as opposed to the idea of the complexity of the elements, which he considered to have been to some extent supported by the periodic law).[165] It is possible that during the early 1860's Mendeleev had not yet rejected the Proutian-type commensurability hypotheses, in which case these would have provided him with grounds for belief in the corresponding protyle hypotheses. By the end of the 1860's, however, Mendeleev had certainly rejected such commensurability hypotheses; and although in 1871 he presented an ad hoc suggestion as to how the corresponding protyle hypotheses might nevertheless be saved, this was intended not as being likely, but merely as being possible in principle.[166]

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[162] The term "unity of plan" (edinstvo plana) is used in this sense on various occasions by Mendeleev himself, e.g. in his Faraday Lecture, 1889 (PLBA, 221).

[163] Pr. Ch. R-1, part II(1871) 834 (main text and footnote); PLBA, 381.

[164] See, for example, Pr. Ch., R-8 (1906) n. 636.

[165] For the details of Mendeleev's attitude regarding the significance of the periodic law for the questions of primary matter and the complexity of the elements, see later.

[166] See Ch.I (section A), and later in the present chapter.

As regards Mendeleev's attitude towards the relevance of the ideas of a single primary matter and the complexity of the elements to chemistry (and to science in general), he appears to have believed during the 1860's and much of the 1870's that it is the central task of chemistry to demonstrate the interconvertibility of the elements, e.g. in 1871 he wrote, "the aim and task [sc. of chemistry] is to transform one [sc. element] into another".[167] After ca. 1880, however, he came to recommend that in the continuing absence of any well-authenticated decomposition, synthesis or transmutation of the chemical elements science should treat the elements pragmatically as qualitatively-distinct ultimate forms of matter. With this recommendation Mendeleev relegated the ideas of a single primary matter and the complexity of the elements from the realms of science to a non-scientific realm which he designated variously as "philosophy", "metaphysics" or "fancy". After ca. 1880, therefore, although Mendeleev still accepted that the elements are probably complex, such a belief had for him become non-scientific. He himself explicitly acknowledged his divided attitude concerning the question of the complexity of the elements during this later period - on the one hand as a scientist, on the other as a "philosopher" - in the following passage written in 1879:

> ... to me personally, as a participant in the discovery of the periodic law of the chemical elements, it would be extremely interesting to assist in the fixing of data for a proof of the transmutation of elements, because I could then hope that the cause of the periodic law would be discovered and understood. Therefore, as a philosopher I pay great attention to every attempt to show the complexity of the chemical elements; but as a scientist I see the futility of all attempts, and therefore ... I try to harmonise the independence of the chemical elements with the other deductions of science.[168]

Mendeleev's attitude from ca. 1880 towards the ideas of a single primary matter and the complexity of the elements appears to provide a prime historical example of a belief in the advantage for science of temporary pragmatism over what is felt to be a premature concern with the question of objective truth.

The motivation which led to Mendeleev's methodological recommendation for science after ca. 1880 that the chemical elements be treated as qualitatively-distinct ultimate forms of matter seems to have been a fear on his part that his newly-established empirically-corroborated periodic

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[167] Diary entry, given in Sc. Ar., 615.

[168] Gold from silver (R.), 1898 written 1897): PLBA, 448.

law might become discredited by association with such speculative ideas as those of a single primary matter and the complexity of the elements.[169] The argument by means of which Mendeleev rationalised his recommendation invoked the demand for unity in nature while requiring also that variety be explained: the source of variety was taken to be the chemical elements, assumed as qualitatively-distinct ultimate entities, and the demand for unity was seen to be satisfied by the periodic law, as a single correlating principle embracing all of the chemical elements.[170] Thus, while Mendeleev sacrificed one aspect of unity in nature (viz. the unity of the matter of the elements) for the sake of the need to explain variety, the demand for unity was nevertheless satisfied in terms of what we might call a "unity of system" of the elements.

The view which Mendeleev held after ca. 1880 concerning the particular nature of the relevance to science of the a priori commitment to the idea of unity is illustrated in the passages given below: these are all extracts from the writings of Mendeleev except for the second passage (of 1886), which is an extract from a report of a communication by Mendeleev to a meeting of the Russian Physico-Chemical Society.

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[169] F.A. Paneth has suggested similarly (Bibl. 90, p.54), "Mendeleeff did not want his discovery to be discredited by having it put on the same level as a philosophic conception handed down from antiquity. He ... therefore tried to draw the dividing line between the periodic system and the idea of primordial matter as sharply as possible".

[170] Alexander Vucinich (Bibl. 126, p. 342) has written: "The philosophical significance of this periodic law ... rests on its recognition of the diversity and the unity of chemical elements as complementary scientific concepts. The diversity of the elements, in Mendeleev's view, is manifested by their unique chemical qualities, the qualities which make them genetically discrete. The unity of the elements, on the other hand, rests on the established fact that each one occupies a definite place in a universal pattern based on ascending atomic weights and the periodic recurrence of similar characteristics."

The picture of the periodic law as a unifying system for qualitatively-distinct elements can be seen as an illustration of the Marxian law of the unity of dialectical contradictions, and has indeed been so interpreted by a number of Soviet historians and philosophers of science. For example, Karpovits and Makarenia have written, "In his scientific work Mendeleev employed many elements of dialectics. He ... criticised metaphysical efforts to reduce the diversity of the universe to a single primary matter... He ... determined the place of each discrete element in a general pattern representing the unity of elements". ("Mendeleev, Dmitrii Ivanovich" in Filosofskaia entsiklopediia, ed. F.G. Konstantinov, Vol. III, Moscow, 1964, p. 386; the translation given here is from Vucinich, Bibl. 126, p. 346).

[1881]... the conviction that primary matter is not so homogeneous as the mind would wish in its original impulse of rapid generalisation is getting stronger from year to year. The unity of laws, the uniformity of the means by which nature formed the simple bodies, is replacing the demonstration of the unity of the material of the simple bodies which is desired by so many people.[171]

[1886]... along with the unity of the law of the elements we should recognise a real difference between the substance of the simple bodies. If there is a demand for seeking and assuming unity in subjects which are being compared, then there must inevitably exist a demand for seeking and assuming causes of independence - otherwise the reason for the difference is inconceivable ... Therefore to exclude by a single intellectual act the existence of every independent individualisation is a mistake; guided by experiment, we ought to admit the variety of the elements, while recognising their subordination to a common law ... It is impossible to see in motion alone the basic cause for material differences without the recognition of the independence of the elements.[172]

[1886-7] The unity of matter is an axiom (aksiom) of the present time. But where is the root of that variety which we meet around us in the world? ... Variety becomes possible if we assume, besides a general unity, such degrees of difference as exist between the simple bodies. By recognising the simple bodies as the final limit of divisibility of substance, we understand that, even if the simple bodies are few, we may obtain from them a huge variety. In this respect chemistry provides many examples; thus, only a few elements ... are sufficient to give the numerous organic compounds. It therefore seems to me that the tendency to seek the unity of matter, so frequently recurring in the history of science, is nothing but a residue of that epoch of thought when it was necessary ... to convince people of unity, and it was not necessary to understand variety.[173]

[1889] When we look for the origin of the idea of a unique primary matter, it is easy to see that, in the absence of inductions from experiment, it originates from the scientifico-philosophical

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[171] Pr.Ch., R-4, part I (1881) 53, footnote; PLSM, 371.

[172] J. Russ. Phys-Chem. Soc., 18, no. 1, section 1, pp. 66-7 (1886); PLBA, 439. The last sentence of this passage seems to represent another example of how Mendeleev tends to overstate his position in a polemical situation (see p.29 for an example of this in connection with Mendeleev's assessment of the atomic theory). In the spirit of Mendeleev's own matter-plus-motion ontology it would seem to be quite possible to explain the variety of the elements in terms of variety of internal motion of a single type of primary matter.

[173] Lectures on theoretical chemistry to higher courses for women (R), 1886-7. PLSM, 248-9; Colls., 15, 460-1.

tendency to seek a unity in the diversity which occurs in the world around us ... By responding to this same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of substance,[174] and the convincing arguments of modern science compel everyone to believe in these kinds of unity. But while we admit unity in many respects, we must also explain the individuality and apparent diversity which is everywhere revealed to us ... So we must say - "Give us something that is individualised, and the apparent diversity will be easily understood". Otherwise, how could that which is unified result in a multitude?[175] After a great toil of researches, natural science has discovered the individualities of the chemical elements, and therefore it is now capable not only of analysing, but also of synthesising; it can understand and grasp not only that which is general and unified, but also that which is individualised and multifarious. The general and unified - such as time and space, or force and motion - varies gradually, permitting interpolation, revealing all intermediate phases. But the multifarious and individualised - such as ourselves, or the simple bodies of chemistry ... - is characterised in another way: we see in it, side by side with a connecting general principle, leaps, breaks in continuity, ... an absence of intermediate links. Chemistry has found an answer to the question of the causes of multitudes; and by retaining the conception of many elements, which are subjected to the discipline of a general law, it offers an escape from the Indian Nirvana - the absorption in the universal - replacing it with the individualised. However, the place for individuality is so limited by the grasping, all-powerful universal, that it constitutes no more than a point of support for the understanding of multitude in unity.[176]

[1903(1905)] Being unable to conceive the formation of the known elements from hydrogen, I can neither regard them as being formed from the element x, even though it is the lightest of all the elements.[177]

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[174] It is highly unlikely that Mendeleev here means "unity of substance" in the sense of the existence of a single primary matter, since he is arguing in this passage against such an assumption in science: in the paragraph immediately preceding the passage quoted here he even characterises the idea of a single primary matter as "this relic of the torments of classical thought". He is probably using the expression "unity of substance" to refer to the fact that all heavenly bodies appear (according to spectroscopic data) to be composed of the same substances (cf. the passage of 1871 quoted above, p.83).

[175] In the spirit of Mendeleev's own matter-plus-motion ontology, but contrary to what he appears to be suggesting here, "that which is unified" could "result in a multitude" by means of variety of internal motion of a single type of primary matter (see also n. 172, above).

[176] Faraday Lecture, 1889: PLBA, 221-2. This passage is quoted by Mendeleev in Principles of Chemistry, R-7 (1902-3) and R-8 (1906). In R-8, n.636, Mendeleev appends the following remarks to the quoted passage: "To what I said more than 16 years ago I now want to add, first, that in science as in life the general is everywhere entangled and linked with the particular, that we cannot intelligently think of man himself in uniformity, without differences of sex, age, means, talents, etc.; and secondly, that the tendency towards unity in everything ... must somehow be reconciled with the variety of particularities, parts and even forms, which are presented everywhere and in everything, because living realism demands this".

[177] Element "x" is the hypothetical element which Mendeleev places in the position "0-0" in the periodic table, and which he tentatively identifies with the luminiferous world-ether (see Ch. I, section C; and Ch. VI, section C).

> I cannot admit this idea, not only because there is nothing which suggests the possibility of the transformation of one element into another, ... but chiefly because I do not see that such an assumption would in any way benefit or simplify our understanding of the bodies and phenomena of nature. And when I am told that unity in the material of which the elements have been built corresponds to an aspiration for unity in all things, then ... I say that it is simpler to assume the germs of individuality in the material elements than in anything else; and we can in no way accept generality without some individuality.[178]

In the last of these passages Mendeleev gives two reasons for rejecting the idea that the hypothetical lightest element "x" (tentatively identified with the luminiferous world-ether) is the sole primary substance: first, the empirical immutability of the chemical elements; and secondly, that it is simpler to admit the germs of individuality in the elements than to postulate the existence of a single primary substance. Earlier in the same article Mendeleev rejects the idea that the ether might be the sole primary matter, on the basis of what appears to be the (fallacious) argument that whereas the ether must be extremely unreactive in order to permeate all bodies easily, any primary matter must possess chemical reactivity in order that the chemical reactions of the elements might be understood: "besides there being no chemical evidence, there can be no real conception of the ether as primary substance because substances must possess ... chemical relations ... for the understanding of the majority of phenomena ... proceeding at immeasurably small distances commensurate with the size of ... the atoms".[179] Mendeleev here seems to have become temporarily blind to the fact that a distinction may be drawn between "primary" and "secondary" qualities.

The details of Mendeleev's views on the significance or otherwise of various "empirical" factors for the questions of a single primary matter and the complexity of the elements may be conveniently presented within the framework given in section A.

a) Simple commensurability of atomic weights: "Prout's hypothesis".

The earliest passage in which Mendeleev expresses an opinion on "Prout's hypothesis" seems to be the following, dating from 1864:

> ... there is even the likelihood that all our simple bodies are not simple, and may, with the advance of science, be decomposed into elements which are still more primary. This view has frequently been expressed in science, a particular corroboration of it appearing to be the multiple-relationship of the atomic weights of those simple bodies to the atomic weight of hydrogen (e.g. the atomic weight of oxygen is 16 times that of hydrogen, sulphur 32 times, iodine 127 times, and so on, so that in general the atomic weights of the simple bodies are whole numbers).

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[178] Attempt at a chemical conception of the world-ether (R), 1903; 2nd edn., 1905. PLBA, 500.

[179] PLBA, 479.

> This multiple-relationship is one of the main arguments upon which chemists who assume complexity of the so-called simple bodies rely. Solely on the basis of this argument they construct theories such as that which assumes the origination of the simple bodies from a condensation of hydrogen atoms, or of some other kind of atom completely unknown to us. But this has not yet led to anything in practice, and has no significance whatever until confirmed by indisputable experiments. So far not a single simple body has been decomposed so as to obtain from it hydrogen or any other substance, and views which have not been factually proved we should accept only when there exist precise rational arguments (ratsional'nye dokazatel'stva) for them. But in any case the multiple-relationship of the atomic weights of the simple bodies to that of hydrogen will not serve as a rational argument for the theory which has been based upon it.[180]

What Mendeleev means in the last sentence of this passage is not at all clear. He seems to have not yet rejected PCH (1; H=1) - "in general the atomic weights of the simple bodies are whole numbers";[181] and it is difficult to believe that he can be claiming that confirmation of PCH (1; H=1) would not provide any sort of evidence for PPH (1H) - not only because of his consistent explicit remarks to the contrary from 1871 onwards, but also because of his apparent statement to the contrary earlier in this very passage of 1864 ("a particular corroboration of it appearing to be the multiple-relationship of the atomic weights"). There seems to be no elucidation elsewhere in Mendeleev's writings of what he might mean by "rational argument" in the present context.

Mendeleev's next reference to "Prout's hypothesis" was the bare comment of 1869 that the periodic system "shows the inadequacy of the hypothesis of Prout".[182] There is no indication of whether Mendeleev is here referring to Prout's commensurability hypothesis, to the protyle hypothesis, or to both; nor does Mendeleev explain why he considers the periodic system to demonstrate "the inadequacy of the hypothesis of Prout".

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[180] Bibl. 75, pp. 16-17.

[181] Makarenia (1965, Bibl. 60, p.41) quotes K.A. Timiriazev (1890) on the question of Mendeleev's attitude towards Prout's hypothesis in the early 1860's: "But meanwhile it is remembered that at the beginning of the '60's in lectures on theoretical chemistry he [sc. Mendeleev] was completely sympathetic towards the hypothesis of Prout, and was as if regretful that the more precise numbers of Stas compelled its rejection".

[182] Report of the 2nd Congress of Russian Scientists and Physicians (for 23rd Aug., O.S., 1869), Moscow: PLBA, 606; Sc. Ar., 75.

In a paper published in 1870 Mendeleev drew a certain analogy between Mg and NaH, and between Ca and KH:

> Sodium is monoatomic [sc. monovalent]; it forms the compounds Na_2O and NaHO. Its atomic weight is 23. Magnesium is diatomic [sc. divalent] and forms an oxide MgO; its atomic weight is 24. One atom of oxygen in magnesium oxide is combined with 24 parts by weight of magnesium; one atom of oxygen in sodium hydroxide is combined with 23 parts by weight of sodium and one part of hydrogen. Magnesium is equivalent to hydrogenated sodium, and even equal to it in weight. Similarly, calcium (40) is identical in weight to potassium hydride KH (39 + 1), and combines, like the latter, with one atom of oxygen. This is as if to show that calcium is a compound of hydrogen with potassium.[183]

Similar remarks are to be found in all eight editions of Principles of Chemistry.[184] Despite their superficial suggestion of a degree of sympathy with PPH (1H), such passages are fairly clearly intended by Mendeleev to have no more than a formal significance, being "completely hypothetical"[185] and not suggesting that Mg is actually composed of Na and H, or Ca of K and H. The "NaH" and "KH" to which Mendeleev refers in these passages are not meant to be the free hydride compounds of sodium and potassium, but merely the two-atom constituent parts of NaOH and KOH.[186]

Mendeleev's attitude towards "Prout's hypothesis"[187] from 1871 onwards is readily discernible from his writings of this period, and may be summarised as;

i) rejection of PCH (1; H=1), and all other testable simple commensurability hypotheses such as PCH ($\frac{1}{2}$; H=1) and PCH ($\frac{1}{4}$; H=1), on the basis of Stas' experimental results of 1860;

ii) acknowledgment that if PCH (1; H=1) or some other simple commensurability hypothesis had in fact turned out to be true, then this would have provided strong corroborative evidence for the corresponding protyle hypothesis;

iii) recognition that refutation of a simple commensurability hypothesis does not necessarily imply refutation of the corresponding protyle hypothesis,

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[183] On the quantity of oxygen in saline oxides (R.), J. Russ. Ch. Soc., 3 (1870) no. 1, 14-21; p.21, footnote. PLBA, 58, footnote.

[184] See, for example, Pr.Ch., R-1, part II (1871) 122; R-8 (1906) Ch.XIV.

[185] 1870: PLBA, 58, footnote.

[186] Before the early 20th century Mendeleev tended to take the formulae of the free hydride compounds of Na and K to be of the type M_2H (see Ch. V, section D-1).

[187] The actual expressions "Prout's hypothesis" (gipoteza Pruta, or gipoteza Prouta) and "Prout's law" (zakon Pruta) tend to have been used by Mendeleev to denote only PCH (1; H=1).

because the building of chemical atoms from protyle atoms may be accompanied by a breakdown in the law of conservation of weight.

Aspects i) and ii) are given undiminishing expression by Mendeleev right up to 1906. Aspect iii), however, was explicitly expressed by Mendeleev only during the period 1871-82, although there are still traces of this idea in certain passages which he wrote in the early 20th century;[188] in his Faraday Lecture, 1889, Mendeleev outlined a closely related conjecture (albeit as "a fantasy of one of my students").[189] Mendeleev's seeming reluctance to express this ad hoc "non-conservation of weight" conjecture after 1882 is probably to be explained in terms of his general tendency from ca. 1880 to dismiss hypotheses about a single primary matter and the complexity of the elements from the realms of science.

One of the fullest accounts by Mendeleev of his views on "Prout's hypothesis" was given in a passage which first appeared in the 1st edition of Principles of Chemistry (1871), and which was retained, with certain modifications, in all of the 7 subsequent editions of this work to be prepared by Mendeleev.[190] In the 1st edition the passage runs as follows:

> Prout ... has maintained that the atomic weights of the elements are multiples of the atomic weight of hydrogen. The subsequent determinations of Berzelius, Penny, Marchand, Marignac, Dumas, and especially Stas, showed this conclusion to be untenable ... Marignac and Dumas ... then claimed that the atomic weights of the elements are expressed in relation to hydrogen either by whole numbers or by numbers containing the simple fractional magnitudes $\frac{1}{2}$ and $\frac{1}{4}$; but Stas' researches, which were carried out with the greatest accuracy, refute this supposition also. Even between the atomic weights of hydrogen and oxygen - judging from the investigations of Dumas and Erdmann - there is not that simple relation which is required by Prout's hypothesis.[191] This hypothesis, for the establishment or refutation of which so many researches have been made, is extremely important, and fully deserves the attention which has been given to it. Indeed, if it were shown that the atomic weights of all the elements may be expressed in whole numbers in relation to hydrogen, or if they at least proved to be commensurable with one another, then it could be affirmed with confidence that the elements, with all their material diversity, were formed of a single material condensed, or grouped, in various modes into the stable and - under known conditions - undecomposable groups which we call the atoms of the elements. At first it was even supposed that the elements are nothing but condensations of hydrogen; but when it was shown that the atomic weights of the elements cannot be expressed by whole numbers in

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[188] PLBA, 326 (see Ch. I, p. 25).

[189] PLBA, 224 (see Ch. I, p. 25).

[190] See, for example, Pr. Ch., R-8 (1906) n.636 (PLBA, 451-2).

[191] Actually, although the data obtained by Dumas (with Stas) on the O:H ratio in 1842 seemed at first not to support PCH (1; H=1), after certain corrections which Dumas deemed justified the ratio did in fact turn out to be integral (see p.61).

relation to that of hydrogen, it was nevertheless still possible to assume that there exists a certain material from which hydrogen and all other simple bodies were built ... Assuming the atomic weight of this material to be unity, then the weights of all atoms must be expressed by whole numbers[192] ... Let us suppose the atomic weight of one element to be m, and of another to be n, then since m and n must be whole numbers it follows that the atomic weights of all elements must show a simple multiple-relationship, i.e. the atomic weights of all elements would be commensurable. But it is sufficient to glance over the results obtained by Stas, and to be assured of their accuracy, especially for silver, in order to destroy completely this attractive hypothesis. So, at the present time we must refuse to assent to the suggestion of the complexity of the known simple bodies. The hypothesis is not supported either by any known transmutation (for one element has never been converted into another element), or by the commensurability of the atomic weights of the elements. The hypothesis can neither be denied nor accepted for want of sufficient data. Marignac, however, endeavoured to overcome Stas' conclusions as to the incommensurability of the atomic weights by supposing that in his determinations, as in the determinations of all other observers, errors had slipped in which were entirely independent of the observer[193] ... Marignac upholds this supposition by the fact that the conclusions of Stas and other observers regarding the most accurately investigated of the atomic weights are extremely close to what Prout's hypothesis demands, i.e. the atomic weights are close to commensurability ... But Marignac's supposition does not endure criticism, although it is extremely sharp-witted. Indeed, if we express the atomic weights of the elements determined by Stas in relation to hydrogen, then the approximation of the atomic weights to whole numbers already disappears, because one part of hydrogen combines (soedinyaetsya) in reality not with 16 parts of oxygen, but with 15.96 parts[194] ... Marignac's arguments cannot serve as a support for the vindication of Prout's hypothesis. We must not conclude from this, however, that the simple bodies are completely distinct in their nature, and have no commensurability whatever, because there is no possibility of verifying such a conclusion.[195]

Immediately after the corresponding passage in the 2nd edition (1873) of Principles of Chemistry Mendeleev added the following comments, which

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[192] There is no suggestion in this passage from Pr.Ch., R-1, of the idea that the weight of a chemical atom might not equal the sum of the weights of its component protyle atoms. The influence of this idea in Pr.Ch. is seen most strongly in R-2, R-3 and R-4 (1873-82) (see below).

[193] See Marignac's paper of 1860, Bibl. 95.

[194] Mendeleev presumably does not really mean "combines" here; but the point does not depend upon this.

[195] Pr.Ch., R-1, part II (1871) 250-2; Colls., 14, 245-7. The last sentence of this passage ("We must not ... conclusion") does not appear in the 5th (1889) and later editions of Pr.Ch. (R).

were retained (with a few insignificant changes of wording) in the 3rd (1877) and 4th (1882) editions, but subsequently omitted:

> Indeed, the conception of the identity of the material which forms all simple bodies - that cherished thought of many investigators - is closely linked historically with the conception of conservation of weight. We may imagine that both phenomena - the conservation of weight and the undecomposability of the simple bodies - are in a dependence of a kind such that with the transition of one simple body into another there is a change in weight. Such an assumption is no more daring than the assumption of the transmutation of one element into another. Both have not been reproduced in reality, both are conceivable; but neither deserves consideration at the present time, because there are other sufficiently important ideas which are worthy of elaboration not only because of their own interest, but also because they allow experimental testing.[196] Prout's law has served as a cause for elaborating our knowledge of atomic weights, but has not itself been retained; and the work of Stas should be considered the final word in the history of Prout's law.[197]

Mendeleev's earliest (and most detailed) explicit publication of his view that the law of conservation of weight might break down in the case of a transmutation of the elements had appeared in 1871. The core of the relevant passage has already been quoted in Ch. I (p.25); its immediate context was as follows:

> Everyone knows the fate of Prout's hypothesis. When investigations forced us to accept fractional numbers for the atomic weights, and when Stas showed that we cannot even assume rational fractions, then, despite Marignac's brilliant critique, there remained no doubt that Prout's hypothesis departed greatly from the facts. It seems to me that there are not even theoretical grounds for the acceptance of Prout's commensurability hypothesis. Even if we agree that the matter of the elements is all of the same kind ... [etc. as on p.25]... we cannot deny that weight may be created or diminished. By this means it is possible to some extent to explain the difference in the chemical energy of the elements. In expressing this idea I wish only to show that there is a certain possibility of reconciling the cherished thought of chemists regarding the complexity of the elements with the denial of the hypothesis of Prout.[198]

Mendeleev's reference here to Marignac's "brilliant critique" of Stas' results is a very strong indication that his "non-conservation of weight" hypothesis was stimulated by the similar conjecture presented by Marignac in this very critique of 1860 (see earlier, p.63).

b) Decomposition, synthesis or transmutation of the elements.

Although Mendeleev did not consider a demonstration of the decomposition, synthesis or transmutation of the chemical elements to be

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[196] Mendeleev is undoubtedly including the periodic law among these "other sufficiently important ideas". We are here already seeing the beginning of Mendeleev's pragmatic dismissal of the ideas of a single primary matter and the complexity of the elements from science.

[197] Pr.Ch., R-2, part II (1873) 238; PLSM, 303.

[198] Loc. cit. (see p.25, n.13).

the only kind of empirical factor which could indicate the complexity of the elements or the existence of a single underlying primary matter,[199] he nevertheless appears to have felt that it would be only on the basis of evidence of this kind that we could conclusively establish such an hypothesis. But Mendeleev never accepted any of the demonstrations which were claimed in this direction, not even those involving the "electronic" and radioactive phenomena observed in the late 19th and early 20th century. He wrote in his Attempt at a chemical conception of the world-ether (R.; 1903, 1905), "In the 50 years during which I have carefully followed the chemical literature, many ... transmutations of certain simple bodies into others have been described; but in each case ... there has been proved either the simple error of prejudice, or insufficient accuracy of research ..."[200] and in Pr.Ch., R-8 (1906) we find the remark that "no such transmutation (of one simple body into another) has ever been demonstrated sufficiently convincingly".[201] Consequently, throughout his career Mendeleev regarded the hypotheses of a single primary matter and the complexity of the elements as lacking definite empirical proof; and he never relinquished the position which, as a chemist, he had adopted by the 1880's, of treating the chemical elements pragmatically as distinct ultimate forms of matter. In 1897 he wrote: "... no-one has ever come across a single phenomenon where one simple substance has changed into another, from which is drawn the conjectural conclusion which is assumed as the foundation of the whole of our science: the chemical elements are independent, and by means of them we must set the limits of our knowledge of the transmutation of substances".[202]

During the late 1880's - particularly in a lecture course of 1886-7[203] and in his Faraday Lecture of 1889[204] - Mendeleev criticised Lockyer's claim that spectral data showed the dissociation of chemical elements in the sun. Mendeleev's criticisms were based upon contributions by Zöllner (1871)[205] and by Kleiber (1885):[206] Zöllner had shown that the

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[199] I am here using the term "empirical" in the sense in which it is used in section A of this chapter, not according to any usage of this term by Mendeleev.

[200] PLBA, 478-9.

[201] PLBA, 525.

[202] Gold from silver (R): PLBA, 447.

[203] See PLSM, 244 ff.; Colls., 15, 455 ff.

[204] See PLBA, 220.

[205] Ueber den Einfluss der Dichtigkeit und Temperatur auf die Spectra glühender Gase, Ann. der Physik, 142 (1871) 88-111; Phil.Mag., 41(1871)190-205

[206] J. Russ. Phys-Chem. Soc., 1885, p.147.

spectrum of an incandescent gas varies with the temperature and pressure of the gas, and with the thickness of the layer of the gas; Kleiber had utilised Zöllner's results, and had considered in addition the different Doppler shifts in the spectra of differently-moving layers of the same type of gas. In his Faraday Lecture Mendeleev concluded his remarks on Lockyer's suggestion that iron is decomposed at the temperature of the sun with the comment, "Moreover, we should not forget that a proof of the decomposition of iron into two or more unknown elements must increase the number of known elements, not decrease it - still less decrease it to a single primary matter".[207] This comment provides a good illustration of Mendeleev's recognition of a distinction between the ideas of a single primary matter and the complexity of the elements.[208]

Late in 1897 Mendeleev wrote an article entitled Zoloto iz serebra (Gold from silver)[209] in which he outlined the researches of S.H. Emmens earlier in the same year on the conversion of silver into gold, and discussed certain questions arising from Emmens' work. Mendeleev related how Emmens had claimed to have achieved a partial conversion of silver into gold, via an intermediate substance "argentaurum"[210], by the alternate action upon the silver of heat and cold, or by prolonged sharp beating of the silver with a hammer.[211] It was in this article that Mendeleev explicitly distinguished the "philosophical" and "scientific" aspects of his own attitude towards the question of the complexity of the elements; and, writing in his "philosophical" vein, he had the following to say about attempts (such as that by Emmens) at producing gold from silver -

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[207] PLBA, 220.

[208] A little further on in his Faraday Lecture (PLBA, 222), after discussing the relevance to science of the demand for unity, Mendeleev again shows that he does not conflate the questions of a single primary matter and the complexity of the elements: "Having touched upon the metaphysical basis of the idea of a unique primary matter composing all bodies, I consider it necessary to dwell also upon another idea, related to the above conception, viz. the idea of the complexity of the simple bodies of chemistry" (Mendeleev then goes on to discuss the work of Pelopidas).

[209] Zh. zhurnalov i Entsiklopedicheskoe obozrenie, St. Pet., 1898, no. 1, pp. 1-11; PLBA, 439-50.

[210] "Argentaurum" was also the name which had been adopted by the American business syndicate for which Emmens was working on this project of transmuting silver into gold.

[211] See PLBA, 439-444.

Being ... not opposed to, but rather inclined to accept, the idea of the complexity of the elements, I can nevertheless in no way side with the alchemists and Emmens when they seek to obtain gold from silver or from some other such metal. This apparent contradiction I shall explain shortly, but first I shall point out that the proof of the complexity (viz. the containing of oxygen) of that which before Peligot was considered to be metallic uranium,[212] did not serve to unsettle the conception of the elements, but served only to advance the knowledge of uranium - just as any isolated transmutation of one metal into another would serve only to advance the stock of chemical knowledge,[213] and could not disturb its harmonious totality. It is necessary to make this remark for those people (fortunately few) who suppose that the scientific edifice of our time is precarious,[214] and could be shaken by a syndicate seeking only profit.

As regards the obtaining of gold from silver: apart from other factors, and assuming the idea of the complexity of the elements, then until we come across the reverse transition - i.e. until we obtain silver from gold - the obtaining of gold from silver seems to me to be extremely unlikely. The fact is that gold has an atomic weight ... of about 197 and a specific gravity in the metallic state of about 19.3, silver having an atomic weight of about 108 and a specific gravity of about 10.5, i.e. for both relationships silver is lighter than gold by nearly a half. And this, judging from all that we know, and assuming the complexity of the elements, compels us to think that gold should be more complex than silver; in the case of the polymers of ethylene and all other gases, for example, the complexity

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[212] Peligot's demonstration that what had been regarded as metallic uranium was in fact uranium oxide, and his preparation of uranium metal, had been in 1841: Compt. rend., 12 (1841) 735; 13 (1841) 417.

[213] Mendeleev is here placing some sort of limitation upon the significance for the elements in general of an isolated case of transmutation; but the specific nature of this limitation is not clear, because Mendeleev does not indicate exactly to what kinds of isolated transmutation he is referring. If we take him to be referring merely to cases of transformation of the type achieved by Peligot, then what he says is unremarkable and perfectly acceptable, because such transformations are completely explicable as special cases in terms of the current conception of the immutability of the elements, as instances of the decomposition of substances hitherto erroneously classed as elements (such as the case of the rare-earth "element", "didymium" - see Ch. VII). However, Mendeleev's next sentence ("It is necessary ..." etc.) seems to suggest that he would also include as an example of an "isolated transmutation" the conversion of silver into gold. If this is indeed so, then I would consider Mendeleev's remarks here to represent a weak and unacceptable "conventionalist stratagem" designed to undermine in advance the importance for our conception of the elements in general of any eventual isolated transmutation of one recognised element, with its own well-established place in the periodic table, into another element with a different well-established place in the periodic table.

[214] This is a reference to the syndicate "Argentaurum" for which Emmens had worked.

> increases with molecular weight, as does the density.[215] Even the melting-point of gold (about 1070°C) is higher than for silver (about 970°C), just as for higher polymers it is higher than for lower polymers. And if we consider that gold is more complex than silver, then we should expect - again, according to the sum of existing chemical knowledge - that gold will more easily change into silver than the reverse,[216] and that both transmutations will occur if the less complex can change into the more complex. This seems to me so probable that, if what Emmens maintains should be confirmed, then I shall search for methods of changing gold into silver ...[217]

In his later comments on the questions of primary matter and the complexity of the elements Mendeleev frequently cited Emmens as an example of a contemporary scientist who had carried out experiments to induce transmutation of one element into another.[218] He referred a number of times in his writings of the early 20th centure also to the work of F. Fittica (1900), for example in the following passage:

> Phosphorus and hence also its preparations, usually contain arsenic. It may be separated from solutions of phosphoric acid by sulphuretted hydrogen. This induced Fittica (1900) to assume that he had succeeded in partly converting phsophorus into arsenic. C. Winkler afterwards proved that this was only a repetition of the mistake which has often given rise to the notion of the elements being transmutable into each other. Such mistakes are likely often to recur in insufficiently careful researches.[219]

Mendeleev's attitude towards the "electronic" ideas of the late 19th century and early 20th century was expressed in the foreword of the 7th (1902-3) edition of Principles of Chemistry as follows:

> The return to electrochemism which is so apparent in the supporters of the hypothesis of "electrolytic dissociation",[220] and the notion of the disintegration of atoms into "electrons", in my view only complicates and in no way elucidates so real a matter (since the time of Lavoisier) as the chemical changes of substances, which have led to the recognition of the elementary weight-bearing and invariable atoms of the simple bodies.[221]

This passage is not found in the 8th (1906) edition of Pr.Ch. However, in this later edition there appears, elsewhere in the book, a new passage (quoted earlier, p.46), in which Mendeleev considers the threat

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[215] Mendeleev is here drawing an analogy between silver and gold on the one hand, and organic polymers on the other, from the structural point of view.

[216] Contrast the view of Samuel Brown, 1841 (see section B of this chapter, p.72).

[217] PLBA, 448-9.

[218] See, for example, Pr.Ch., R-7 (1902-3) foreword, n.6; Colls., 24, 43.

[219] Pr.Ch., E-3 (Kamensky's translation from R-7), II, 190, n.14.

[220] In talking of a "return to electrochemism" Mendeleev undoubtedly has in mind the earlier electrochemical views of Berzelius. For a further comment by Mendeleev on "electrolytic dissociation" see Ch. I, n.87.

[221] Pr.Ch., R-7 (1902-3): Colls., 24, 43.

to chemical atomism from the ideas of the "electronicists" and "energeticists", and dismisses such ideas as having no advantage over chemical atomism for the understanding of the chemical elements.[222] Also in the 8th edition of Pr.Ch. Mendeleev notes that "according to many present-day scientists (Crookes, J. Thomson, Lord Kelvin and others, especially among the English) the atoms of the simple bodies break up under certain conditions into primary ultimate parts (electrons, radiant matter, protyle, etc.)", commenting merely that "we are here evidently close to the very boundary of modern knowledge; ... there are in this field many possibilities, but no certainties" (op.cit., p.483; PLBA, 600).

Mendeleev was never convinced that radioactivity is accompanied by a change of one element into another.[223] In 1904, commenting upon the discovery by Ramsay and Soddy (1903) of the production of helium from radium, he suggested that the helium which was produced had originally been in occluded combination with the radium:

> ... there have appeared certain new investigations on radium ...; ... this concerns the giving off of helium (Ramsay), and the observation of the spectrum of this element in the light emitted by radium (Huggins), but in my opinion we cannot see in this anything so significant as is assumed by certain people, who are acquainted with this subject to only a small extent, because the helium may be in absorbed (occluded) combination with the radium; there are no grounds to think that there is a transformation of radium into helium.[224]

Mendeleev later remarked upon another observation made by Ramsay and Soddy in the same series of experiments, viz. the emergence of the spectrum of helium in a collected sample of radium "emanation". Mendeleev considered this result inconclusive because of the extremely small quantities of materials involved:

> Those gases which are given off from preparations of radium and other similar radioactive substances carry the general name "emanation"

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[222] Mendeleev did not suggest any explanation of the "electronic" phenomena of the discharge tube, but it is probable that he felt the likely explanation to be in terms of the "ether" (just as he postulated the existence of an "ethereal" mechanism for the electrical effects associated with radioactivity - see Ch. I, section C).

[223] In addition to presenting a tentative qualitative explanation of radioactivity in terms of his "chemical conception" of the luminiferous world-ether (see Ch. I, section C), Mendeleev also suggested - drawing a general analogy with magnetism - that perhaps radioactivity is a "property or state" which can be induced in various (but not all) substances under appropriate conditions (see, for example, Pr.Ch., R-8, 1906, n.565; PLBA, 526).

[224] Elements (chemical)(R.), in Bibl. 11, vol. 40, half-vol. 80, 1904, p.634, footnote (PLBA, 419-20, footnote).

... Ramsay and Soddy (1903-1904) showed that with the passage of time emanation shows the spectrum of helium (and also of CO and CO_2). It seems that experiment ... suggests that emanation ... suffers change in time. To speak categorically about ... this ... seems to me most premature, because the phenomena are unexpected, and the quantities with which the experiments have so far been carried out - even for the compounds of radium themselves, not to mention the emanations given off by them - have been limited, by lack of material, to only a few milligrams.[225]

Ramsay (1903) observed the emergence of the spectrum of helium in a collected sample of emanation of radium, and saw in this observation the transmutation of one element into another. But it may be that the helium was simply in the radium, and was given off from it with the emanation.[226] The question is extremely important, but its precise experimental investigation is not possible until[227] radium is obtained in quantities allowing precise measurements.

At the same time Mendeleev had the following to say in connection with certain claims made by Boltwood:

Boltwood (1905) has quantitatively determined the radioactive capacity of 22 minerals containing uranium, and has found that it corresponds exactly to the content of uranium. He therefore maintained that radium is produced by uranium; and because all uranium ores contain some lead, he also proposed that Pb is the final product of the gradually proceeding transformations of uranium. This is all connected with the idea of the unity of matter; but no such transformation (of one simple body into another) has ever been demonstrated sufficiently convincingly. I consider it my duty to state clearly in connection with this, that in my attentive study of the numerous memoirs concerning radium I have so far not come across a single phenomenon which could provide a definite demonstration of the transformation of radium into any other element; nor, speaking generally, have I come across any cases of the transformation of one element into another. Many experiments require checking; some of these experiments indicate a series of phenomena which are of course at present inexplicable because of their having been only poorly studied, and because of the great rarity of the starting materials.[228]

c) Analogy of the elements with compound radicals and with organic compounds.

Mendeleev seems to have felt that although certain analogies between the elements on the one hand, and the compound radicals (both inorganic and

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[225] Pr.Ch., R-8 (1906) n.565; PLBA, 527.

[226] Such an explanation hardly explains the observation by Ramsay of the gradual appearance of the spectrum of helium for an isolated sample of emanation which originally showed no helium spectrum.

[227] Pr.Ch., R-8 (1906) n.565; PLBA, 528.

[228] Pr.Ch., R-8 (1906) n.565; PLBA, 525.

organic) and organic compounds on the other, were to some extent indicative of the complexity of the elements, this evidence could not from a scientific point of view be regarded as strong. Mendeleev's references to analogies of the elements with the compound radicals and organic compounds were much more frequent during the earlier part of his career - broadly speaking before ca. 1880 - than during the later part.

In 1862 Mendeleev pointed to analogies between the elements and the organic radicals in the following passage:

> Like the organic atomic radical, a group which does not decompose in the majority of reactions and passes from one compound to another, so are atoms ... they pass from one body to another without decomposition. A confirmation of this view can be seen in the parallelism in the relationship of the composition of simple and complex radicals. It was long ago observed that complex organic radicals differ from each other by the same constant value, e.g. it is always $CH_2 = 14$ for the homologues. The same kind of difference is shown by the simple bodies such as Cl, Br, I, K, Na, Li, etc. Though we have no proof that the simple radicals are complex.[229]

In 1870 Mendeleev again implied a structural analogy between chemical elements and organic radicals when he wrote: "... just as certain members of homologous series are not obtained, ... for example, methylene ..., perhaps the elements of low atomic weight from 1 to 7, i.e. between H and Li, may be impossible."[230] In 1871 he drew a structural analogy between families of chemically-similar elements and series of organic polymers, on the grounds that just as, for example, $C_{16}H_{32}$ and C_2H_4 both combine with Cl_2, but $C_{16}H_{32}$ much less energetically than C_2H_4, so also the heavier elements of a series of chemically-similar elements, while giving the same types of reaction as the lighter elements, do so less energetically.[231]

In 1897 Mendeleev suggested a structural analogy between Ag and Au on the one hand and organic polymers on the other (see above, n.215 and the quoted text to which it refers). However, most of Mendeleev's few considerations after the early 1880's of analogies between the elements and the compound radicals or organic compounds tended to be concerned with the parallelism observed by Pelopidas (1883) between the periodicity of the

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[229] This passage is an English translation given in Journal of Inorganic Chemistry, USSR (from Zh. Neorg. Khimii, vol. II, No. 4, 1957, pp. 712-718), p.2, of a quotation from Mendeleev's lectures on theoretical chemistry (1862) in a paper by S.A. Shchukarev entitled Sovremennaia neorganicheskaia khimiia v svete idei D.I. Mendeleeva (Modern inorganic chemistry in the light of the ideas of D.I. Mendeleev).

[230] PLBA, 99.

[231] Diary entry, 1871: Sc.Ar., 617. Also, Pr.Ch., R-1, part II (1871) 834; PLBA, 381.

of the elements and certain periodic relationships among organic radicals:[232] although he acknowledged this parallelism as having some (unknown) significance for the question of the cause of the periodic law,[233] Mendeleev did not accept it as providing an argument for assuming the complexity of the elements in chemistry.[234]

Recognition by Mendeleev that a complexity of the elements is to some extent suggested by the analogies existing between the properties of certain elements on the one hand and certain inorganic radicals on the other is to be found in the first four editions of Principles of Chemistry (1869-81), but not in later editions. In the first four editions of Pr.Ch., after discussing the strikingly similar properties shown by potassium and ammonium in their alums Mendeleev remarks that from this fact "the possibility arises of thinking that the simple bodies themselves may in due course be decomposed", although he immediately adds, "The latter supposition we can in no way accept as completely certain, however".[235] His greater reluctance by ca. 1880 to suggest that such analogies indicate a complexity of the elements is clearly evident in the 4th edition of Pr.Ch.(1881), where we find also the following passage:

> ... if MCN, HCN, HCNO, etc. were known without there being known any instances either of the formation of the compounds from carbonaceous or nitrogenous substances, or of their decomposition into nitrogen and carbon rather than cyanogen, then we would count cyanogen also as a simple body. The weights CN=26, F=19, Cl=35.5 are all large; perhaps they contain the atoms of other, lighter elements, H, C, N, O, or others. All this is to some extent conceivable, possible. But not all that is possible is true, and many even probable things turn out to be far from the truth; and there is at present no basis

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[232] When discussing Pelopidas' work Mendeleev sometimes refers in passing also to the related work of Carnelley (1886) (see, for example, PLBA, 222).

[233] For example, in Pr.Ch., R-7 (1902-3) Ch.XV, n.11, Mendeleev wrote: "With regard to this remarkable parallelism it must be noted that, for the elements, with the transition to neighbouring members with higher valency the atomic weight increases, whilst here [sc. for the organic radicals] there is a decrease in weight; but everything indicates that the periodic variability of simple and compound bodies is subject to some higher law, the nature and cause of which there is at present no means of understanding ...".

[234] See his Faraday Lecture: PLBA, 222-4.

[235] Pr.Ch., R-1, part I (1869): Colls., 13, 75. Also in R-2, R-3, R-4.

> for maintaining the existence in F, Cl, etc. of any other simple bodies, whereas there is complete certainty in the complexity of composition of CN.[236]

d) The periodic law.

As also was the case the the "philosophical" demand for unity in nature (see earlier), the periodic law possessed a two-fold significance for Mendeleev in connection with the ideas of a single primary matter and the complexity of the elements, influencing on the one hand his opinion concerning the objective truth of these ideas, and on the other hand his opinion (from ca. 1880) concerning their relevance to science.

In 1871 Mendeleev explicitly acknowledged that the periodic law appears to provide corroboration of the idea of the complexity of the elements, although he gave no reasons for this conclusion:

> ... at present it is not yet possible to offer any hypothesis which sufficiently explains this law of periodicity ... It is easy to assume - but not yet possible to prove, perhaps even quite wrong, and in any case still subject to great doubt - that the atoms of the simple bodies are complex entities formed by the combination of still smaller parts (ultimates[237]), that those entities which we call indivisible (atoms) are indivisible only for normal chemical forces, just as molecules are indivisible under ordinary conditions by physical forces; however, despite the precariousness and arbitrariness of such an assumption,[238] the mind which is acquainted with chemistry is involuntarily inclined towards it. That is why such a doctrine has reappeared in various forms over many years, and the periodic dependence between properties and weight, proposed by me, evidently corroborates this presentiment (if we may call it such) which is so characteristic of chemists.[239]

This appears to be the only passage dating from the era of Mendeleev's discovery of the periodic law (1869-71) where he is definitely considering the question of the significance of this law for the ideas of primary matter and the complexity of the elements.

In Mendeleev's writings after the 1870's there seem to be only two passages where he gives any indication of his attitude towards the

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[236] Pr.Ch., R-4, part I (1881) 519; PLSM, 371-2.

[237] In a diary entry made at about the same time as this passage was written, Mendeleev wrote: "Beyond the limits of O and H, are ultimates (ul'timaty)" (Sc.Ar., 611).

[238] Mendeleev here appends a footnote about the basis of the assumption of "ultimates" beyond the chemical atoms - "Which assumption takes its basis from a comparison with the form of the universe ..." (etc., as quoted earlier, p.83).

[239] Pr.Ch., R-1, part II (1871) 834; PLBA, 380-381.

significance of the periodic law for the question of the objective truth of the ideas of a single primary matter and the complexity of the elements.[240] Both these passages were written towards the end of 1897 (in different articles). In one, Mendeleev talks (albeit explicitly as a "philosopher" rather than as a "scientist") about his hope that a proof of the complexity of the chemical elements - i.e. a decomposition, synthesis or transmutation of some sort - would lead to an understanding of the cause of the periodic law, which at least indicates that he did not at this time consider the periodic law to provide evidence against the objective truth of the idea of the complexity of the elements:

> If it were to be shown [sc. that the elements are not immutable]..., then we may gain the possibility of understanding the lawfulness which has been noticed for the elements, namely their periodicity ... Thus, to me personally, as a participant in the discovery of the periodic law of the chemical elements, it would be extremely interesting to assist in the fixing of data for a proof of the transmutation of elements, because I could then hope that the cause of the periodic law would be discovered and understood. Therefore, as a philosopher I pay great attention to every attempt to show the complexity of the chemical elements...[241]

In the other passage of 1897 Mendeleev claimed that the periodic recurrence of the properties of the elements with increasing atomic weight provides evidence against the hypothesis of a single primary matter:

> ... I am not able to consider that the periodic law serves as an indirect confirmation of the idea of the unity of matter - i.e. that all the elements are stable (under existing conditions) polymers, or forms of equilibrium with different degrees of condensation, of one and the same primary matter - because then as the weight increases we would consequently expect an entirely uniform change of properties, and not a recurrence of the initial kinds of change.[242]

I am reluctant to accept that these two passages are contradictory, for the following reasons: first, they were written at almost exactly the same time; secondly, it is clear that by this time Mendeleev appreciated that although the concepts of a single primary matter and the complexity of the elements are related, they are not identical;[243] and thirdly, Mendeleev's argument in the second of the passages quoted does not actually mention the idea of the complexity of the elements as distinct from that of a single

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[240] I do not include in this category certain remarks by Mendeleev where he seems to suggest (fallaciously) that the justification which the periodic law provides, as a "unity of system", for pragmatically assuming the chemical elements to be qualitatively-distinct ultimate forms of matter has some significance also for the question of the objective truth of the ideas of a single primary matter and the complexity of the elements (see later; and also n.172, above).

[241] Gold from silver (R): PLBA, 447-8. (A continuation of this passage is quoted on p.84).

[242] Bibl.11, vol. 23, half-vol. 45, 1898, 318 (PLBA, 258).

[243] See n. 208, above.

primary matter - in fact it would be much less convincing as an argument against the complexity of the elements than it is against the existence of a single primary matter.[244] It therefore seems justifiable to conclude that in 1897 Mendeleev (as a "philosopher") considered the periodic law to be perfectly consistent with - and perhaps even indicative of - the complexity of the elements, while at the same time he felt that this law provided a certain amount of evidence against the existence of a single primary matter.

As regards the part played by the periodic law in connection with Mendeleev's assessment (from ca. 1880) of the relevance to science of the ideas of a single primary matter and the complexity of the elements, this was two-fold: on the one hand it seems to have been a fear that the periodic law would be discredited by association with such speculative ideas which originally led Mendeleev to dismiss these ideas from the realms of science; and on the other hand it was the periodic law, as a single correlating principle embracing all of the elements, which provided an empirical basis for his methodological argument for science that the chemical elements be treated pragmatically as ultimate, thus rationalising his dismissal from science of the ideas of a single primary matter and the complexity of the elements.

Some of Mendeleev's comments during the 1880's criticising those who took the periodic law as evidence for a single primary matter or the complexity of the elements are presented in two passages below. The first-quoted passage (of 1886) was not written by Mendeleev himself: it is an extract from the report of a communication by Mendeleev to a meeting of the Russian Physico-Chemical Society. The second passage is from Mendeleev's Faraday Lecture (1889). Both passages reflect a tendency by Mendeleev at this time to suggest (fallaciously) that the justification which the periodic law provides (as a "unity of system") for pragmatically rejecting the ideas of a single primary matter and the complexity of the elements from science, has some significance also for the question of the objective truth of these ideas.[245]

[1886] D.I. Mendeleev speaks out against the application by

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[244] The compound organic radicals, composed of two types of constituent (C and H), had already been shown by Pelopidas (1883) and Carnelley (1886) to exhibit a certain periodicity, as Mendeleev knew.

[245] See n. 240, above.

Mr. Rantsev,[246] as also by many others,[247] of the periodic law for the induction of the unity of the matter which forms the elements. Mendeleev at present, as also at the time of his establishment of the periodic law,[248] is inclined, rather, to see in this law an induction to the recognition of the distinct independence (individuality, variety) of the elements, along with the rule of a general law...[249]

[1889] ... the modern adherents [sc. of the "Pythagorean idea" of the unity of matter] have become so convinced of its confirmation by the periodic law that the illustrious Berthelot, in his interesting book "Les origines de l'Alchimie" ..., has simply mixed up the fundamental idea of the periodic law with the ideas of Prout, the alchemists, and Democritus concerning a single primary substance. The periodic law, being based upon the solid and wholesome ground of experimental investigation, has arisen completely independently of any idea about the nature of the elements; it does not at all originate from the conception of the unity of the matter of the elements, it has no historical connection with this relic of the torments of classical thought. It is therefore as little indicative of the unity of matter and the complexity of the elements as are the law of Avogadro-Gerhardt, the law of specific heats, or even the conclusions of spectroscopy.[250]

e) Spectroscopic data

Mendeleev's earliest expression of an opinion on the origin of line-spectra appears to have been in the 3rd (1877) edition of Principles of Chemistry:

If every salt of Na, of Li, of K, gives one and the same spectrum, then this must be ascribed to the presence in the flame of the free metals, produced by decomposition of the salts ... In my opinion the modern state of the question of spectra may be expressed in the following way: spectral phenomena are determined by molecules, and not by atoms, i.e. the molecules of metallic sodium, and not the atoms of sodium, produce that family of vibrations which is expressed in the spectrum of sodium. Where there is no free sodium metal, there is no sodium spectrum.[251]

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[246] A manuscript article on the periodic law by Rantsev is to be found in Mendeleev's personal library (I-160/12a) in the Mendeleev Museum-Archive, Leningrad University.

[247] Mendeleev here appends the footnote: "For example, Ciamician. Berthelot in his book on alchemy (Les origines de l'Alchimie) also erroneously attached to the periodic law the tendency to indicate the possibility of the transmutation of the simple bodies".

[248] The historical accuracy of this remark is, I feel, questionable (see earlier).

[249] PLBA, 438. A continuation of this passage is quoted on p.86.

[250] PLBA, 220-221. A continuation of this passage is quoted on pp. 86-7.

[251] Pr.Ch., R-3 (1877) 763. Mendeleev appears to have considered the "conclusions of spectroscopy" not to have indicated the existence of a single primary matter or the complexity of the elements (see below); and apparently similarly for "the law of Avogadro-Gerhardt" and "the law of specific heats".

This conception of line-spectra as originating from molecules of simple substances rather than from atoms of elements was retained by Mendeleev throughout his life,[252] which helps to explain why he never acknowledged that spectral data provide evidence of the complexity of the elements.[253] However, it is difficult to see how Mendeleev could have reconciled this latter position with his molecular theory of spectra in the case of the mercury spectrum. He had accepted the monoatomicity of mercury vapour as early as 1860,[254] and he certainly knew of the existence of the mercury spectrum; perhaps he simply never seriously considered the significance of the existence of this spectrum. A similar problem arises for the case of the inert gases, the monoatomicity of which Mendeleev came to accept in 1900.[255]

Towards the end of 1880 Mendeleev received two letters from Ciamician in which the latter presented the view, based upon his observation of "homologous spectra", that the different elements of a given natural group are composed of the same kind of matter.[256] Mendeleev replied to

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[252]For example, in Pr.Ch., R-7 (1902-3) 412, he wrote "If every salt of Na, of Li, of K, gives one and the same spectrum, then this must be ascribed to the presence in the flame of the free metals, produced by decomposition of the salts. Therefore spectral phenomena are determined by entire molecules, and not by the atoms they contain, i.e. the molecules of metallic sodium, and not the atoms of sodium, produce that family of vibrations which is expressed in the spectrum of sodium salts. Where there are no free molecules of sodium metal, there is no sodium spectrum, although there may be sodium atoms". In Pr.Ch., R-8 (1906) Ch. XIII, the corresponding passage ends at the words "determined by entire molecules".

[253]He did, however, acknowledge that spectral data may have some bearing upon certain (unspecified) theoretical problems in chemistry: "It may be hoped that in time spectroscopic researches will clarify certain aspects of the theoretical (philosophical) demands of chemistry, but all that has been done so far in this respect can only be regarded as attempts which have not yet given any completely definite conclusions" (Pr.Ch., R-5, 1889, 416; also in R-6, R-7, R-8).

[254]See Colls., 15, 170.

[255]See Ch. VII.

[256]The "homology" of spectra referred to the occurrence of analogous spectra (i.e. analogous series of lines) for the different elements of a given chemical family, with the entire spectrum progressively shifted in going from one member of the family to the next.

In his first letter to Mendeleev, Ciamician said: "the cause of the homologous spectra of the elements of the natural groups should be sought in the fact that such elements consist qualitatively of the same kind of matter" (MALU: see Makarenia, Bibl. 60, pp.35-6). In his second letter Ciamician wrote: "... it seems to me that in general it can be acknowledged as a true hypothesis, that the cause of the homology of the spectra must be sought in their [sc. the elements'] similarity of substance. This conviction has been strengthened in me because of the correspondence of the homology of the spectra of the elements and the regularities of their atomic weights" (MALU: see Bibl.60, p.36).

Ciamician criticising this view.[257]

In his Faraday Lecture (1889) Mendeleev criticised Lockyer's claims that spectral data indicate a dissociation of certain elements under the extreme conditions existing in the sun (see earlier), and also criticised the suggestion which had been made by various scientists (e.g. by Crookes, 1886) that spectral "helium" is perhaps the sole primary matter of the universe:

> As soon as spectral analysis appears as a new and powerful weapon of chemistry, the idea of primary matter is immediately attached to it. From all sides we see attempts to find the so-much longed-for primary matter in the imaginary substance helium. No attention is paid to the fact that the helium line is seen only in the solar protuberances,[258] so that the question of the general occurrence of helium in nature is as problematic as that of primary matter; or to the fact that the helium line is not seen among the Fraunhofer lines of the solar spectrum ...; or, finally, to the fact that experiment clearly shows that the intensity of the light of the spectral lines of the simple bodies varies with differences of temperature and pressure. And therefore we may think that the helium line belongs to some long since known element placed under such conditions of temperature, pressure and gravity as have not yet been realised in our experiments.[259]

Mendeleev's continuing refusal to accept that spectral data provide a key to the solution of the question of the nature of the elements was clearly expressed in the early 20th century - with apparently even greater conviction than previously - in a passage found in the 7th (1902-3) and 8th (1906) editions of Principles of Chemistry: "... the more I have thought about the nature of the chemical elements, the more firmly have I turned away from the classical notion of primary matter, and from the hope of attaining the desired end by a study of electrical and optical phenomena".[260]

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[257] Mendeleev's reply was to Ciamician's first letter, prompting the second letter from Ciamician. Mendeleev's letter seems not to have survived.

Later, Mendeleev was to write (Pr.Ch., R-7, R-8; e.g. R-8, n.368): "... a germ of the understanding of the link between atomic weights, chemical analogies, and the positions of the spectral lines of the simple bodies is apparent; but in my opinion we do not yet see the precise laws which govern the dependence of the said subjects, but we see only a reflection of the periodic law." By "reflection of the periodic law" Mendeleev is here referring to the periodic recurrence of similar spectra for analogous elements.

[258] Helium was discovered on the earth in 1895 (by Ramsay).

[259] PLBA, 219-220. Mendeleev's comments on Lockyer's claims follow on from the passage quoted here.

[260] Pr.Ch., R-7 (1902-3): Colls., 24, 42. The corresponding passage from R-8 (1906) has "the desired understanding of the nature of the elements" instead of "the desired end": Colls., 24, 51.

f) Other, miscellaneous, empirical factors.

There are two points which seem worthy of mention here. First, whereas certain chemists in the 19th century considered the phenomenon of allotropy to suggest the unity of matter, Mendeleev's clear distinction between "simple body" ("simple substance") and "element" ruled out such a belief on his part. And secondly, we have seen that in 1863 Graham expressed the view that "The essential unity of matter is an hypothesis in harmony with the equal action of gravity upon all bodies"; what appears to be a similar view is presented by Mendeleev in the 7th (1902-3) and 8th (1906) editions of Principles of Chemistry - "With the consolidation of the periodic law the almost-forgotten idea of primary matter out of which all the simple bodies are supposed to have been made has become more and more frequently revived. This seems to me to be perfectly natural if mass be considered as directly dependent upon the quantity of substance".[261]

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[261] PLBA, 326. The underlining is mine, not Mendeleev's.

CHAPTER III

THE EMERGENCE OF THE PERIODIC LAW OF THE CHEMICAL ELEMENTS (EARLY 19th CENTURY TO 1871)

A. Introduction

In this chapter is presented a largely factual sketch of those developments which occurred during the sixty or so years up to 1871 in the investigation of atomic-weight relationships and the classification of the chemical elements, from which eventually emerged in the 1860's the discovery of the periodicity of properties of the elements. We recognise the actual "era of discovery" of the periodic law as being 1862-71, beginning with the contribution of de Chancourtois in connection with his "vis tellurique", and terminating with the publication of Mendeleev's long article in Liebig's Annalen on The periodic lawfulness of the chemical elements (Nov. 1871; G.).[1]

Of major significance for the emergence of the periodic law was the development and clarification of concepts of a characteristic weight of the elements - of the concepts of "equivalent weight" and "atomic weight". The values of such characteristic weights provided the basis for numerous attempts at classifying the chemical elements during the half-century which preceded the discovery of the periodic law. Also of significance for the emergence of the periodic law was the development and use of concepts which came to be clarified in that of "valency": the development of the concept of valency was intimately linked with that of the concepts of atomic weight and equivalent, leading to an awareness of the relationship, valency = $\frac{\text{atomic weight}}{\text{equivalent}}$; and the recognition of chemical families involved to an appreciable extent classification according to valency. The construction of the periodic system represented the culminating synthesis of the hitherto only partially correlated approaches of classification according to characteristic weight and according to chemical

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[1] There already exist various accounts in English of the history of the developments which led to the emergence of the periodic law, of particular note being those by Venable (Bibl. 124) and Spronsen (Bibl. 110). Only in connection with the contributions of Mendeleev does the content of the present chapter go beyond these existing accounts to any appreciable extent.

A convenient and useful collection of facsimile reprints of certain relevant primary material is given in Bibl. 47.

family, as a correlation of atomic weight and valency for all of the elements.[2]

The first attempt at drawing up a list of atomic weights appears to have been Dalton's Table of the relative weights of the ultimate particles of gaseous and other bodies, probably dating from 1803 (the year in which he had developed his atomic theory).[3] In calculating his "relative weights" (based upon H=1) Dalton adopted an empirically unfounded simplicity criterion for deciding the formulae of compounds.[4] Other tables were published by Dalton in his New System of Chemical Philosophy in 1808 and 1810.[5]

Also in 1810, T. Thomson published a list of equivalents in his System of Chemistry.[6] This contained only very few equivalents of elements, dealing mainly with acids and bases. A decided improvement upon Thomson's list was Wollaston's table of equivalents of 1814.[7] Wollaston preferred to

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[2]C.A. Russell (Bibl. 100, p.139) has concluded that, unlike the case of the classificatory systems based upon atomic weight, "it does not seem that the systems based upon valency were of great influence upon the development of the Periodic Law. The part played by valency in this was recognised after it had been established from a study of atomic weight relationships." In talking of "systems based upon valency" Russell seems to be considering only those classifications of the 1860's which were based explicitly upon valency ("atomicity"), such as that by Williamson in 1864 (J. Chem. Soc., 17, 211). However, to separate such attempts - on what are largely no more than terminological grounds - from the various attempts at classification according to chemical family which were made during the 1850's and even earlier, is rather misleading for an understanding of the trends from which the periodic law emerged. The tendency to classify elements into chemical families was certainly "of great influence upon the development of the Periodic Law"; and such a tendency involved to an appreciable extent classification on the basis of what by the 1860's had come to be called "atomicity", and which was soon called "valency".

[3]This table was published in Mem. Lit. Phil. Soc. Manchester [2], 1 (1805) 287, as part of a lecture entitled The absorption of gases by water and other liquids which Dalton had read in 1803. However, Roscoe (Chem. News, 30, 1874, 266-7) considered that the atomic-weight values published with the lecture may have been obtained after the lecture had been given.

[4]Roughly speaking, Dalton assumed compounds to have the simplest possible formulae, e.g. HO for water. For different compounds of the same two elements he assumed successively the formulae AB, AB_2, A_2B, etc.

[5]Part I, London, 1808; part II, Manchester and London, 1810.

[6]4th edition, Edinburgh, 1810, vol. V.

[7]A Synoptic Scale of Chemical Equivalents, Phil. Trans. Roy. Soc., 104 (1814) 1.

work with equivalent weights rather than with the more "theoretical" atomic weights, considering the former to be of greater practical value. Wollaston's view was favourably received by many chemists, such a reaction being encouraged by Gmelin's preference for equivalents in the first three editions of his Handbuch.[8]

In 1814 Berzelius published his first atomic-weight values; these were revised by him in 1818, and also in 1826.[9] In drawing up his table of 1826 Berzelius utilised two new discoveries which greatly aided him in establishing which particular multiple of the equivalent should be taken as the atomic weight of an element, viz. Dulong and Petit's law of constant "atomic heat" (1819), and Mitscherlich's law of isomorphism (1819-20). In 1828 two lists of atomic weights were published by Dumas,[10] the second of which showed fairly close agreement with Berzelius' 1826 list.

In 1811 Avogadro had published his now famous hypothesis, "le nombre des molécules integrantes dans les gaz quelconques, est toujours le même à volume égal" ("the number of molecules in any gas is always the same for equal volumes"),[11] which provided the basis upon which a satisfactory molecular theory could have been built. In 1814 this same hypothesis was proposed by Ampère.[12] However, the hypothesis was largely ignored until Cannizzaro emphasised its importance at the Karlsruhe Congress of 1860. Consequently, until the 1860's ideas regarding molecules generally remained in a state of confusion. The resulting uncertainty concerning molecular weights often made it difficult to decide which multiple of the equivalent weight of an element represents its atomic weight.

Notable among the few chemists apart from Cannizzaro who appreciated the significance of Avogadro's hypothesis before 1860 were Laurent and Gerhardt, particularly the former (who attributed the hypothesis to Ampère).[13]

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[8] Handbuch der theoretischen Chemie, 2 vols., Frankfurt am Main, 1817-9; 2nd edn. 1821-2; 3rd edn. 1827-9.

[9] Ann. Phil., 3 (1814) 362. Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité, 1819, pp. 122-151. Ann. Phys., 7 (1826) 397-416; 8 (1826) 177-190.

[10] Traité de Chimie, Paris, 1828, vol. I, pp. XXXII and L.

[11] Journal de Phys., 63 (1811) 58-76.

[12] Ann. Chim., 90 (1814) 43.

[13] From 1826 until 1832 Avogadro's hypothesis had been accepted by Dumas, who then discarded it because of anomalous results from vapour-density measurements; these results are retrospectively explained by dissociation of the gases investigated. An appreciation of Avogadro's hypothesis was shown by Mendeleev from 1856 (see later).

In 1842 Laurent emphasised that "atom" and "equivalent" are not identical, and that the equivalent of an element can vary.[14] In the following year Gerhardt published two papers on the "equivalents" of the elements[15]; the values of these so-called "equivalents" actually corresponded, with a few exceptions, to the values of Berzelius' atomic weights. Early in 1846 Laurent clearly distinguished "atom", "molecule" and "equivalent"[16], after which time Gerhardt also recognised such distinctions.[17]

In 1858 Cannizzaro published a paper entitled Sunto di un corso di filosofia chimica fatto nella Reale Universita di Genova.[18] This began with the remarks:

> I believe that the progress of science made in these last years has confirmed the hypothesis of Avogadro, of Ampère, and of Dumas on the similar constitution of substances in the gaseous state; that is, that equal volumes of these substances, whether simple or compound, contain an equal number of molecules, not however an equal number of atoms, since the molecules of the different substances, or those of the same substance in its different states, may contain a different number of atoms, whether of the same or of diverse nature.[19]

Cannizzaro went on to say that the hypothesis of Avogadro and Ampère "contains nothing contradictory to known facts, provided that we distinguish, as they did, molecules from atoms".[20] On the question of the application of the hypothesis to the determination of molecular weights he wrote:

> On the basis of the hypothesis cited above, the weights of the molecules are proportional to the densities of the substances in the gaseous state. If we wish the densities of vapours to express the weights of the molecules, it is expedient to refer them all to the density of a simple gas taken as unity, rather than to the weight

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[14] Revue Scient., 6 (1842) 76-99.

[15] Ann. Chim., 7 (1843) 129-143; 8 (1843) 238-245.

[16] Ibid., 18 (1846) 266-298.

[17] For example, in Introduction à l'Étude de la Chimie par le Système Unitaire, 1848 (dedicated to Laurent). Gerhardt was greatly influenced by Laurent, as has been shown by Clara de Milt: J. Chem. Ed., 28 (1951) 204; Chymia, 4 (1953) 107.

[18] Il Nuovo Cimento, 7 (1858) 321-366. This paper was reprinted as a separate pamphlet in 1859 (Pisa) and in 1880 (Rome). A German translation appeared in Ostwald's Klassiker, no. 30, 1891; an English translation is given in Bibl. 12 (as Sketch of a course of chemical philosophy given in the Royal University of Genoa), and extracts in English translation are included in Bibl. 57 (under the title Abridgement of a course ..., etc.). Partington (Bibl. 92, p. 491) translates the title as Epitome of a course ..., etc.

[19] Bibl. 57, pp. 407-8.

[20] Ibid., p.408.

> of a mixture of two gases such as air ... Whoever wishes to refer the densities to hydrogen = 1 and the weights of the molecules to the weight of half a molecule of hydrogen, can say that the weights of the molecules are all represented by the weight of two volumes.
>
> I myself, however, for simplicity of exposition, prefer to refer the densities to that of hydrogen = 2, and so the weights of the molecules are all represented by the weight of one volume.[21]

Later in the Sunto Cannizzaro stated his "law of atoms":[22] "The different quantities of the same element contained in different molecules are all whole multiples of one and the same quantity, which, always being entire, has the right to be called an atom".[23] Expressing the same idea in what he called less "hypothetical" language, Cannizzaro wrote:

> The various quantities of the same element contained in equal volumes either of the free element or of its compounds are all whole multiples of one and the same quantity; that is, each element has a special numerical value by means of which and with the help of integral coefficients the composition by weight of equal volumes of the different substances in which it is contained may be expressed.[24]

Cannizzaro's main contributions in his Sunto to atomic-molecular theory may be summarised as follows:

i) the clear recognition of the distinction between "atom" and "molecule";

ii) the use of Avogadro's hypothesis to determine molecular weight; and iii) the determination of atomic weights from molecular weights using the "law of atoms" (now sometimes known as "Cannizzaro's Principle"[25]).

Cannizzaro's Sunto did not gain immediate widespread recognition; and by 1860 the general situation in the field of atomic weights, molecular weights and molecular formulae was so confused that Kekulé proposed that an international congress be held to attempt a clarification of such subjects. In conjunction with Weltzien and Wurtz, Kekulé contacted the most prominent European chemists of the time, seeking their support for the scheme. The response was favourable; and announcements of the Congress, to be held in Karlsruhe in September, 1860, were duly sent out in July, 1860. The announcements included an outline of the proposed programme: "... through a thorough discussion many misunderstandings might be removed; especially an agreement in regard to the following main points might be made easier:

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[21] Ibid., pp. 410-11.

[22] Ibid., p. 415.

[23] Ibid., pp. 412, 414.

[24] Ibid., p.415.

[25] For example, see Bibl. 92, p. 491.

More precise definitions of the concepts of atom, molecule, equivalent, atomicity, alkalinity, etc., discussion on the true equivalents of bodies and their formulas; initiation of a plan for a rational nomenclature ...".[26]

The Congress was held on September 3rd, 4th and 5th, 1860. The official report was written by Wurtz. Wurtz states that about 140 chemists attended, of whom he lists 127[27]; among those listed are Gladstone, Odling, Dumas, Strecker, Foster, Marignac, Stas, Lothar Meyer, Mendeleev, Kopp, Roscoe and Bunsen.[28] Another report of the Congress which appeared was a letter from Mendeleev (dated 7th Sept., 1860, Heidelberg) to his former teacher Voskresenskii, which was published in the Sankt-Peterburgskie Vedomosti (St. Petersburg Gazette), no. 238 (Nov., 1860).[26] Extracts from this report by Mendeleev are given below:[30]

> Kekulé had initially proposed many questions for solution: the question of the difference between molecule, atom and equivalent; the question of atomic-weight values, i.e. of whether to accept the atomic weights of Gerhardt, or those of Berzelius, which have subsequently been altered by Liebig and Poggendorf, and which most people accept at present; further, the question of formulae, and, finally, even the question of those forces which, in the present state of science, we need to take as the cause of chemical phenomena. But at the first session, on September 3rd (new style), the meeting considered it impossible in the short time to clarify such a large number of questions, and therefore it was decided to settle for the first two only.
>
> ... After lengthy discussions, the meeting decided to elect a committee, numbering 30,[31] to determine in what form the questions should be put to the Congress for voting. The committee - the Russians in which were Zinin, Shishkov and myself - met immediately after the end of the first session. The committee soon came to the conclusion that the whole essence of the disagreements is concentrated in the distinction between the ideas of molecule and atom. As soon as this distinction is recognised, then that doubling of formulae which

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[26] Given in Bibl. 15 (translated from the German version of the announcement).

[27] See Bibl. 15.

[28] Dumas did not arrive until the afternoon of the 2nd day of the Congress (4th Sept.). Among those who did not attend were Newlands and de Chancourtis (see later, section C); nor were there any Americans present.

[29] Reprinted in Colls., 15, 165-174.

[30] Certain extracts from Mendeleev's report are included in English translation (by H. Leicester) in Bibl. 15, translated from extracts given by B.N. Menshutkin in Bibl. 79. Unfortunately, however, in Bibl.15 these extracts are interspersed with translations of Menshutkin's summary of parts of Mendeleev's report, presented as though they were direct quotations from Mendeleev.

[31] Mendeleev here appends a footnote: "There were in all about 150 people at the meeting. From Russia there were: Zinin, Shishkov, Borodin, Natanson, Savich, Lesinskii and myself".

constitutes the subject of disagreements in the practice of science is immediately allowed. It was therefore unanimously decided to propose the first question for voting in the Congress thus: does the majority wish to assume a distinction between atoms and molecules?

In the discussion on equivalents we had to abandon completely the possibility of attaining any definite conception. Some understood by equivalents the quantities of bodies which substitute each other without change of fundamental properties; others considered equivalents to be the proportions by weight of chemically combining bodies; finally, a third group considered the consistent construction of a conception of equivalents to be quite impossible, to lead without fail to contradictions. Disagreements also complicated the question of molecules. Some admitted only chemical characteristics, i.e. reactions, for the determination of the molecule of each body; others considered that only physical characteristics are needed; and, finally, a third group maintained the identity of both starting-points, ie. they admitted both paths and considered that they will lead to the same results. During these discussions, the most determined and, without doubt, the most original and integral opinion was expressed by the brilliant Professor Cannizzaro...

... Cannizzaro recognised only one method [sc. of arriving at the molecular weight] as being completely reliable. It had been pointed out by Ampère and Avogadro, on the basis of the work of Gay-Lussac, Dumas and Mitscherlich[32]; it was later adopted by Gerhardt and Laurent. This method consists in determining the volume of bodies in the gaseous or vaporous state, i.e. in determining the specific gravity of bodies in such a state ... The principle of volumes ... may be expressed thus: in vapours and gases the distance between the centres of the molecules is the same for all bodies and depends only on pressure and temperature ... Everything we know at present indicates agreement between the weight of molecules as determined by volumes of vapour, and by the quantity of bodies which enters into reaction...

We have so far seen complete agreement between the opinions of Cannizzaro and of Gerhardt and his followers. All that has been said up till now serves only as a clear expression of the doctrine of Gerhardt; I myself have expressed a similar opinion at the beginning of my article (known to you) in the "Bulletin of the Academy" for January 1858.[33] But Cannizzaro, by adhering firmly to the indicated principle, goes further, and points to a notable error made by Gerhardt.

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[32]The history here is somewhat awry. Dumas and Mitscherlich certainly did not lay the foundation for the work of Avogadro (1811) and Ampère (1814); their work came later. (Dumas was only eleven years old in 1811; Mitscherlich was 17).

[33]Mendeleev is here referring to his article Über den Zusammenhang einiger physikalischen Eigenschaften der Körper mit ihren chemischen Reaktionen, Bull. de la Cl. phys.-math. de l'Acad. des Sc., St. Pet., 17 (1858) 49-68.

On the subject of Mendeleev's work during the 1850's in the field of atomic-molecular theory see Bibl. 16 (Dobrotin), Bibl. 107 (Shchukarev and Dobrotin), Bibl. 17 (Faerstein) and Bibl. 18 (Faerstein).

Gerhardt, who nearly everywhere used to take molecules, in the case of metallic compounds took equivalents. On his theory, the formulae of the metallic salts were the formulae of acids in which hydrogen had been replaced by a metal; consequently all metals were monobasic radicals, just like hydrogen. Such an assumption does not have any kind of support; it is simply a concession to the past ...

And so, here is the new conception - the polyatomicity [sc. polyvalence] of metallic radicals. As far as I am aware it was first expressed, with the greatest consistency, by Cannizzaro in his letter to Luca (Nuovo Cimento, VII, fasc. di Maggio, Anno 1858) ...

Cannizzaro's animated speech was, quite rightly, greated with general applause ...

On the next day [sc. 4th Sept.] the committee again met, in order to decide finally in what form it would be most convenient to present the questions to the Congress for voting. It was decided to present the questions in the following form: does the Congress wish, and consider it helpful, to distinguish between the conception of molecule as the quantity of matter entering into reaction and corresponding to the physical properties, and the conception of atom as the smallest quantity of a body entering into molecules? ...

At the second meeting of the Congress, 4th September, ... Kekulé spoke for a long time, disentangling the fundamental conceptions of atoms, molecules and equivalents ... Afterhim, Cannizzaro spoke ... Finally, the Secretary read the questions which had been proposed for voting, in English, French and German. They were -

"It is proposed to acknowledge a distinction between the conceptions of molecule and atom, considering a molecule as the quantity of a body which enters into reaction and which determines physical properties, and considering an atom as the smallest quantity of a body which is contained in the molecules".

Further - "it is proposed to consider the conception of equivalent as empirical, not depending upon the notions of atom and molecule".

The President requested those who accept these propositions to raise their hands. The great majority was seen to accept them. Then it was requested that those who oppose the propositions should raise their hands; a single hand was raised, but then immediately withdrawn. The result was unexpectedly unanimous and significant. By accepting the distinction between atom and molecule, chemists of all countries acknowledged the basis of the unitary system; it would now be a great inconsistency to accept its basis and not accept its consequences.

Towards the end of this meeting Dumas joined us, having just arrived from Paris ...

On the next day [sc. 5th Sept.] the Congress met for the last time ... Dumas proposed that the new atomic weights be used for organic bodies, and the old ones retained for mineral bodies.

Cannizzaro and certain other chemists objected to Dumas' suggestion ...

To this account I add the remark that in all of the discussions there was not a single hostile word between the opposing parties. All this, it seems to me, is a full guarantee of the rapid success of the new principles in the future. Already, out of a hundred and fifty chemists not one has brought himself to vote against these principles.[34]

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[34] Colls., 15, 165-174.

Despite Mendeleev's appreciation of, and enthusiasm for, the views expressed by Cannizzaro at the Karlsruhe Congress, and his optimism with regard to the rapid general acceptance of these views, by no means all of the chemists who attended the Congress were similarly convinced; confusion and misconception still remained in the minds of many.[35] That Mendeleev so quickly and readily accepted Cannizzaro's views was undoubtedly a consequence of the fact that he had himself already been working along similar lines during the period 1856-9, influenced in this respect mainly by the writings of Gerhardt: Mendeleev's work of 1856-9 shows clear signs of his recognition of the distinction between atom, molecule and equivalent, of his acceptance of Avogadro's hypothesis, and of his appreciation of the significance of this hypothesis for molecular-weight determinations.[36]

A factor which probably contributed greatly to the eventual general understanding and acceptance during the course of the 1860's of Cannizzaro's views was the distribution by Pavesi,[37] at the close of the Karlsruhe Congress, of copies of Cannizzaro's Sunto. One of those who received a copy was Lothar Meyer, who later described its impression upon him as follows: "It was as though the scales fell from my eyes, doubt vanished, and was replaced by a feeling of peaceful certainty".[38] Meyer developed the ideas of Cannizzaro in his textbook Die modernen Theorien der Chemie, begun in 1862 and published in 1864.

Cannizzaro's clarification of the concept of atomic weight laid the basis for the establishment during the 1860's of the new system of atomic weights upon which the periodic law was founded.

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[35] See Clara de Milt, Chymia, 1 (1948) 153; and J.W. van Spronsen, Chem. Weekblad, 58 (1962) 484.

[36] Studies of this subject by Dobrotin, Shchukarev and Faerstein are referred to above, n.33.

In general there seems to be little justification for claiming priority for Mendeleev over Cannizzaro with respect to appreciation of Avogadro's hypothesis: not only does Cannizzaro appear to have begun his work in this direction slightly earlier than Mendeleev, but also Cannizzaro's work of the 1850's tends to show a clearer and more complete understanding of the questions involved than does Mendeleev's. However, it does seem that Mendeleev published the formula relating vapour density to molecular weight two years before Cannizzaro (in 1856, compared with 1858 - see especially Faerstein, Bibl. 17, p. 290).

[37] Pavesi and Cannizzaro were the only Italians at the Karlsruhe Congress.

[38] See de Milt, Bibl. 15; and Ostwald's Klassiker, no. 30, 1891, p.59.

B. Attempts at classifying the chemical elements, and at determining numerical relationships between their atomic weights, which were made during the half-century preceding 1862.

A prominent aspect of the history of atomic-weight relationships during the half-century preceding 1862 was provided by the Proutian-type commensurability hypotheses (see Ch. II). These hypotheses had no direct bearing upon the emergence of the periodic law; but insofar as they stimulated accurate atomic-weight determinations they had an indirect influence in this direction. Among the various attempts during the first sixty years of the 19th century at classifying the chemical elements into groups, one of the earliest was that of Ampère, 1816, which had 48 elements arranged into 3 classes on the basis of volatility, fusibility, and colour in solution.[39] Ampère's system, like Prout's hypothesis in the realm of atomic-weight relationships, had little connection with those subsequent classificatory systems - based upon chemical analogy and atomic-weight relationships - which led eventually to the discovery of the periodic law.

The earliest contribution which can be recognised as a direct - albeit distant - precursor of the periodic classification would seem to be the "triad-relationship" discovered by J.W. Döbereiner.[40] In 1816-17 Döbereiner observed that the equivalent of strontium oxide is the arithmetic mean of those of calcium oxide and barium oxide (leading him to suggest that strontium may be some sort of mixture or compound of calcium and barium). Twelve years later (1829) he published his second (and final) article on such "triads". In this 1829 article Döbereiner pointed out that an unpublished prophecy which he had made[41] - viz. that bromine should have an atomic weight equal to the arithmetic mean of those of chlorine and iodine - had been confirmed (to a close approximation) by the value of the atomic weight of bromine obtained by Berzelius.[42] He re-stated the triad-relationship $\frac{CaO + BaO}{2} = SrO$,[43] and gave a number of new triads, e.g. Li-Na-K,[44] S-Se-Te. He felt that F could not belong to the group Cl-Br-I because $Cl \neq \frac{F + Br}{2}$, and that F must therefore belong to a second halogen group,

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[39] Ann. Chim. Phys., 1 (1816) 295-308; 2 (1816) 116-125. Phil. Mag., 47 (1816) 438-446 (given in Bibl. 47, pp. 220-8). See also Bibl. 19, pp. 184-5, and Bibl. 47, pp. 230-2.

[40] See Ch. II, n.90 (p.70) for source-references.

[41] In 1826 or 1827 (see Bibl. 110, p.66).

[42] J.J. Berzelius, Ann. Phys. Chem., 14 (1828) 566. Bromine as a free element (simple substance) was first isolated in 1825, by Löwig and Balard (independently).

[43] Such equations as this are presented here for convenience; they were not given by Döbereiner himself.

[44] In his 1829 paper Döbereiner claims to have recognised this triad in 1817 (see Bibl. 124, p.30).

the two other members of which would be discovered in due course if the law of triads be valid.[45] Döbereiner refused to accept as triads those groups of three elements which showed the "arithmetic-mean" relationship but which are not chemically analogous, e.g. C-N-O (where $N = \frac{C + O}{2}$); such relationships he attributed to chance - as distinct from the triad-relationships of analogous elements, which he considered not to be accidental.

With the exception of certain contributions by Leopold Gmelin, very little attention was paid to the law of triads until the 1850's.

In 1827 Gmelin had proposed two triads, Ca-Sr-Ba and Li-Na-K, the first of which (if not both[46]) had been observed by Döbereiner in 1817. Gmelin also found the following relationship - $\frac{Mg + Ba}{4} = \frac{12 + 68.6}{4} = 20.15 = Ca\ (= 20.5)$. Like Döbereiner, he considered such relationships between chemically-analogous elements not to be accidental.[47]

In 1843 Gmelin extended Döbereiner's work of 1829 on triads, and also tried to find a relationship between all of the elements.[48] One of his attempts in this latter direction led him to a V-shaped classificatory scheme which incorporated 55 different elements.[49] The significance of the particular arrangement of the different families in this system with respect to relationships between the families was not discussed.

In a lecture in 1850 on relationships between the equivalent weights of the elements M. von Pettenkofer criticised the doctrine of triads,[50] attributing to chance the facts that the equivalents of Sr and Br are the arithmetic means of those of Ca and Ba, and Cl and I, respectively.[51] Pettenkofer's own contributions were nevertheless largely extensions of those of Döbereiner and Gmelin: he pointed out that for a family of analogous elements arranged in order of increasing equivalent weight of its

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[45] This seems to have been the earliest prediction of unknown elements on the basis of an observed lawlike relationship among known elements.

[46] See above, n.44.

[47] Handbuch der theoretischen Chemie, 3rd edn., vol. I, 1827, pp.34 ff.

[48] Handbuch der Chemie, 4th edn., vol. I, 1843, pp. 52, 456.

[49] Given in Bibl. 110, p.71.

[50] Pettenkofer did not mention Döbereiner, referring only to Gmelin in this context.

[51] See Ch. II, n.121 (p.75) for source-reference.

members, the difference between the equivalents of consecutive members is frequently equal to 8 or some multiple of 8, and sometimes equal to 5 or a multiple of 5, e.g.[52]

Li = 7	O = 8	C = 6
Na = 7 + 16 = 23	S = 8 + 8 = 16	B = 6 + 5 = 11
K = 23 + 16 = 39	Se = 16 + 24 = 40	Si = 11 + 10 = 21
	Te = 40 + 24 = 64	

In contrast to his dismissal of the law of triads, Pettenkofer did not consider this frequent occurrence of the difference 8, or multiple of 8, to be accidental. However, that this difference of 8 equals the equivalent weight of oxygen he did take to be a coincidence.

In his lecture of 1850 Pettenkofer also drew a parallel between the relationship of the equivalents within a natural group of elements and the weight-relationship within an homologous series of organic radicals.[53] He seems to have been the first to recognise such a parallel. In 1858 Pettenkofer again commented upon the topics which he had considered in 1850, referring to related investigations which had been made since 1850 by Dumas (Pettenkofer, Liebig's Annalen, 1858, 105, pp. 187-202).

At the 1851 meeting of the British Association (at Ipswich), Dumas drew attention to the triads,[54] without, apparently, mentioning those who had contributed earlier to the field; he seems in fact to have been not yet aware of the work of Pettenkofer. Dumas suggested that the intermediate member of a triad may be somehow composed of the two extreme members; and pointed to the possibility of predicting the existence of an unknown middle element of a triad if the two extreme elements happened to be known. Dumas' talk attracted great attention, and was a major factor in arousing the widespread interest which developed during the 1850's concerning relationships among the atomic weights (or equivalent weights), and the possible complexity of the elements.[55] Later in the 1850's Dumas himself contributed greatly to the work on atomic-weight relationships and the classification of the elements (see below).

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[52] During the 1850's boron was commonly assigned - as here by Pettenkofer - to the same "natural family" as C and Si; earlier, Gmelin (1843) had also classified C, B and Si in the same group.

[53] This parallel with the organic homologous series, and also the fact that NH_4 and CN behave very much like elements, led Pettenkofer to believe in the complexity of the elements (see p.75).

[54] Observations on Atomic Volumes and Atomic Weights, with considerations on the probability that certain bodies now considered as elementary may be decomposed. See Ch. II, n.91 (p.70) for source-references.

[55] On the subject of the reaction to Dumas' British Association address of 1851, and concerning its seminal importance in the history of the emergence of the periodic law, see Ch. VIII.

In 1852 P. Kremers pointed out certain relationships between the "atomic weights" of various elements, considering both analogous and dissimilar elements,[56] e.g. he remarked upon the regular difference of 8 weight-units in the series, O(= 8), S(= 16), Ti(= 24.12), P(= 32), Se(= 39.62). Noticing that division of "atomic-weight" values by 4 gave an odd number for metals and an even number for non-metals, Kremers was led to postulate the existence of a fundamental element of "atomic weight" 4. In 1856, on the basis of a belief in the composite nature of the middle element of a triad, Kremers suggested that the deviations of the middle term of certain triads from the arithmetic mean of the extremes are temperature dependent, and at a particular temperature such deviations should disappear.[57] Also in 1856 Kremers combined certain triads into what he called "conjugated triads", e.g. he gave the conjugated triad,

Li = 7	Na = 23	K = 39
Mg = 24	Zn = 40	Cd = 112
Ca = 40	Sr = 87.5	Ba = 137,

where, Li : Na : K = Li : Mg : Ca. He extended this idea to three dimensions, giving "cubic triads" containing 27 elements. He believed that there would be three such cubic triads - one positive, one negative and one intermediate.

In 1853 J.H. Gladstone published a list of the elements (numbering 56 in all) arranged in the order of increasing "atomic weight".[58] Because the "atomic weights" which were used - taken from Liebig's Jahresbericht, 1851 - corresponded in many cased to the incorrect multiple of the equivalent, a periodic recurrence of similar elements was not apparent in this ordering. For example, the first 16 elements in Gladstone's list were:

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[56] Ann. Phys. (Pogg.), 85 (1852) 37, 246.

[57] Ibid., 99 (1856) 58. Kremers still proposed a temperature-dependence of atomic weights in his Physikalisch-chemische Untersuchungen, Vol. I, Unzerlegbare Körper und Verbindungen erster Ordnung, Wiesbaden, 1869/70. Also in this latter publication Kremers presented a classificatory system of the elements (given in Bibl. 110, p.140) which shows certain rudiments of periodicity. By this time, however, greatly superior systems had already been drawn up by Mendeleev and others.

[58] On the Relations between the Atomic Weights of analogous Elements, Phil. Mag. [4], 5 (1853) 313-20. Given in Bibl. 47, pp. 353-60.

1	Hydrogen	14	Nitrogen
4.7	Glucinum [sc. beryllium]	16	Sulphur
6	Carbon	19	Fluorine
6.5	Lithium	20	Calcium
8	Oxygen	21.3	Silicon
10.9	Boron	22.4	Zirconium
12	Magnesium	23	Sodium
13.7	Aluminium	25	Titanium[59]

Gladstone did observe certain irregularities in his list: "If we glance at this list we notice some peculiarities, but no very striking ones. We might ask, for instance, Why should there be so many elements congregated about No. 28 [sc. 'atomic-weight' value 28]; and again, about 52? Why should there be only one atomic weight between 80 and 99, and then a group of four?"[60] He included in his paper a letter which he had received from Augustus de Morgan in which the latter presented a calculation with some bearing upon how to determine the likelihood that such a clustering of atomic-weight values be the result of chance.[61]

Gladstone adopted the V-shaped classification of the elements which was given in Watts' English translation (1849) of the 1843 edition of Gmelin's Handbuch.[62] He recognised three kinds of numerical relationship between the atomic weights of analogous elements: "The atomic weights of analogous elements may be the same; or may be in multiple proportion; or may differ by certain increments".[63] The first kind of relationship - exemplified for Gladstone in the series Cr 26.7, Mn 27.6, Fe 28, Co 29.5, Ni 29.6 - was compared by him to allotropy; the second kind of relationship - "the platinum group has double the atomic weight of the palladium group"[64] - he compared to polymerism; the third kind of relationship, which he saw in the triads, was compared by him to that within the homologous series of organic chemistry. Gladstone acknowledged the earlier work of Gmelin and Dumas on the subject of triads: "See Gmelin's Handbook of Chemistry, part I. Dumas also brought forward some speculations on these groups at the Ipswich Meeting of the British Association".[65] As regards the drawing of an analogy between families of chemical elements (triads) and organic homologous series, it seems that not only did Gladstone arrive at the idea independently (i.e. without any knowledge of Pettenkofer's work), but he may also have been the

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[59] Phil. Mag., 1853, p.313.

[60] Ibid, p.314.

[61] Ibid, pp.314-5. See Ch.II, n.19 (p.57).

[62] Watts had slightly modified Gmelin's classification.

[63] Phil. Mag., 1853, p.317.

[64] Ibid.

[65] Ibid., p.318, footnote. Gladstone had attended the Ipswich meeting of the British Association, 1851.

first to have drawn the attention of Dumas to this idea, at the British Association meeting of 1851. Of particular interest in connection with this latter point is a letter written by Gladstone to Mendeleev many years later (dated 4th Jan., 1890), which contains the following passage:

> In your Faraday lecture you mention M. Dumas as expounding the analogy between the atomic weights of some series of metals (L, Na, K, etc.) and those of homologous organic radicles. Could you oblige me with the reference to his writings on the subject? I believe he first heard the idea from me at Ipswich in July 1851, and I am trying to find out how the idea developed.[66]

The work of J.P. Cooke, 1854-5,[67] resembled that of Pettenkofer, although Cooke seems not to have been aware of Pettenkofer's results. He considered Dumas to be the leader in the study of atomic-weight relationships, and compared his own work to that of Gladstone. Cooke classified all the elements into 6 "series" which he compared to homologous series in organic chemistry. Like Gmelin, Pettenkofer and Gladstone he regarded C, B and Si as homologues. He represented the "atomic weights" of the elements within a given series by a formula for an arithmetic progression, e.g. for the series O(8), N(14), As(75), Sb(129), Bi(208), he gave the formula $8 + n6$, where $n = 0, 1, 4, 11, 20$ and 23 respectively. Insofar as he pointed out that triads break up the natural groups of elements (his "series") he contributed to the overthrow of the doctrine of triads in the sense of the latter as isolated natural groups of elements rather than as parts of larger natural groups. Within his series Cook recognised "sub-series": in this we see the germ of the later recognition of different sub-groups of elements within larger family groups. He considered that one of the most remarkable aspects of his classification was the "affiliation of the series", i.e. the existence of similarities between elements of different series.

In 1857 two papers were published on the subject of triads by E. Lenssen[68]. In the first of these papers Lenssen attempted to extend the doctrine of triads to include all the known elements, presenting in all 20 triads. Some of these triads show little analogy between members, e.g. O-N-C. The order in which Lenssen listed his various triads was not arbitrary: the non-metal triads were listed adjacent to each other, as were the triads of similar kinds of metals; further, certain groups of

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[66] MALU, album 2, document 528. The writings of Dumas to which Mendeleev had referred in his Faraday Lecture were those of the period 1857-9 (see below).

[67] The Numerical Relation between the Atomic Weights, with some Thoughts on the Classification of the Chemical Elements, Amer. J. Sci. (Silliman) [2], 17 (1854) 387-407 (given in Bibl.47); Mem. Amer. Acad. Arts Sci., new series, 5 (1855) 235.

[68] Annalen, 103 (1857) 121; 104 (1857) 177.

3 adjacently-listed triads formed what Lenssen called "enneades", where the middle members of the 3 triads give a new triad. Lenssen's idea of "enneades" is very similar to that of Kremers' "conjugated triads". Lenssen used his doctrine of triads and enneades as the basis for determining certain unknown "atomic weights". For example, triads 4, 5 and 6 in his classification were -

(4)	Mn(27.5)	Fe(28)	Co(29.5)
(5)	La(47.3)	Ce(47)	Di(49.6)
(6)	Yt(32.2)	Er(?)	Tb(?).[69]

On the basis of the enneade, $\frac{\text{triad 4 + triad 5}}{2}$ = triad 6, Lenssen obtained the "atomic weight" of Er as $\frac{28 + 47}{2} = 37.5$. He then obtained the "atomic weight" of Tb from triad 6: $\frac{Yt + Tb}{2} = Er$, therefore Tb = 2Er - Tb = 75 - 32.2 = 42.8. These values for erbium and terbium are quite wrong, even as equivalents and taking into account the terminological inversion.

At the end of his first paper of 1857 Lenssen noted that in every triad two elements more closely resemble each other than the third element, and he represented the third element as a transitional element to the next triad:

(1) K Na } Li
(2) Ba Sr }
(3) Mg Zn } Ca
etc.

In his second paper Lenssen discussed the colour of salts, and of flame spectra, in the context of his doctrine of triads.

In 1857 Odling arranged the chemical elements into 13 "natural families".[70] A few of these families were triads (e.g. Li, Na, K; Ca, Sr, Ba), but most contained more than three elements. Odling noticed that some of the larger groups contained triads plus an extra analogous element whose atomic weight is approximately half the value of that of the first member of the triad, or double that of the last member. He recognised three general types of atomic-weight relationship within groups of analogous elements (acknowledging Gladstone's similar conclusion of 1853): "The most prominent relations which obtain among the elements are the relation of parity or

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[69] Lenssen's "erbium" was what we now call "terbium", and his "terbium" was an impure form of what we now call "erbium". (On the history of erbium and terbium, see Ch. VII).

[70] On the Natural Groupings of the Elements, Phil. Mag. [4], 13 (1857) 423-39, 480-97.

equality, and the relation of series of gradation; but an aliquot or multiple relation is also occasionally manifested".[71] The first four families in Odling's classification were - F, Cl, Br, I; O, S, Se, Te; N, P, As, Sb, Bi; and B, Si, Ti, Sn. Acknowledging that perhaps carbon also should be included in the fourth of these groups, Odling noted:

> The elements fluorine, oxygen, nitrogen and carbon, which would thus stand at the head of the four groups,[72] present a curious numerical sequence:-
>
> C = 12 forms H_4C 5 vols. = 2
> N = 14 " H_3N 4 vols. = 2
> O = 16 " H_2O 3 vols. = 2
> F = 18 " HF 2 vols. = 2.[73]

Towards the end of 1857 Dumas, acknowledging Cooke's similar work of 1854-5, listed a number of series of analogous elements, representing the atomic-weight values of the elements within a given series by means of expressions of such types as a + nd, ma + nd, and a + md + nd', where a, d, d' are constants, and n, m are integers.[74] For example, he gave the series -

N(14)	P(31)	As(75	Sb(119)	Bi(207)	a = 14, d = 17,
a	a + d	a+d+d'	a+d+2d'	a+d+4d'	d' = 44

Like Cooke, Dumas compared such series to homologous series in organic chemistry.

In 1858 Dumas observed a parallelism between different series of elements, e.g. for the two series F-Cl-Br-I and N-P-As-Sb the weight-difference I-F = Sb-N (= 108), Br-F = As-N (= 61), and the weight-differences between the corresponding members of the two families (i.e. F-N, Cl-P, Br-As and I-Sb) are the same, or nearly so (= 4.5 or 5).[75] He went on to talk about the "double parallelism" observed if we arrange the elements into a table such that a given family is placed between two other families, to each of which it shows a parallelism: here, a given element in the central family (apart, presumably, from the lightest and the heaviest elements of the family,

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[71] Ibid., p.424.

[72] Carbon (at.wt.12) would stand at the head of the fourth group because Odling took the atomic weight of boron to be 14.5, corresponding to the formulae BO_2 and BCl_4 for its oxide and chloride.

[73] Op.Cit., p.439. The expressions "5 vols. = 2", etc., indicate the number of "gaseous atomic volumes" of the reacting elements which give two "gaseous volumes" of the resulting compounds. Odling's inclusion of the formula H_4C for methane in this passage represents one of the earliest recognitions of the tetravalence of carbon; the tetravalence of carbon was recognised at about the same time also by Kekulé and by Couper (see Russell, Bibl. 100, pp. 61-80).

[74] Compt. rend., 45 (1857) 709; given in German translation in Annalen, 105 (1858) 74.

[75] Compt. rend., 46 (1858) 951-3; 47 (1858) 1026-34.

although Dumas does not mention this) would be surrounded by 4 other elements which are related to it by analogies of different kinds and different degrees.[76] Dumas did not actually present a classificatory system of such a kind, illustrating this "double parallelism"; nor did he mention the particular order in which he envisaged the various families to be arranged in such a system.

Also in 1858 Dumas again compared the natural families of elements to homologous series of organic radicals, taking this analogy as grounds for belief in the composite nature of the elements. In 1859 he summarised in one article his various contributions to the study of the relationships among atomic weights, particularly emphasising his views as to the probable composite nature of the elements.[77] He also added some supplementary new material, e.g. he suggested new formulae for expressing the atomic-weight values of the elements within certain families.

J. Mercer, in a paper to the British Association in 1858, pointed out many numerical relationships between atomic weights.[78] He also discussed the correspondences between elements and organic radicals, e.g. he made the following comparisons involving the alkali-metal elements -

Li = 7, is like H;

Na = b_2Li_3 = 23, is like C_2H_3 (methyl);

K = b_4Li_5 = 39, is like C_4H_5 (ethyl);[79]

where b = 1. Mercer gave no further explanation of the nature or significance of the component b in the formulae b_2Li_3 and b_4Li_5. Like Dumas, Mercer drew parallels between the fluorine, oxygen, nitrogen and magnesium groups; he represented these relationships schematically in a "table of the Atomic Parallels".[80]

In 1859 N.N. Sokolov expressed the homology within various groups of analogous elements by means of the single general formula, a + nd, where a and d are constants for a given group - a being the atomic weight of the

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[76] Ibid., 953. In discussing "double parallelism" Dumas refers to "metals" (métaux) rather than to "elements" or "simple bodies". However, he seems to be using the term "metals" not in a strict sense, but loosely to denote elements in general.

[77] Ann.Chim.Phys. [3], 55 (1859) 129-210.

[78] Report Brit. Assoc. Adv. Sci. (Transactions), 1858, pp. 57,59.

[79] These formulae for methyl and ethyl are based upon C = 6.

[80] This table is reproduced by Spronsen in Bibl.110, p.92.

first member of the group, and d being an atomic-weight difference characteristic of the group - and n is an integer (cf. the earlier work of Cooke and of Dumas).[81] Sokolov critically analysed the views of Dumas on the nature of the elements.

In 1859 A.F.L. Strecker, who had long had an interest in relationships between atomic weights, summarised the results relating to this subject,[82] concluding, "It is hardly probable that all the above-mentioned relations between the atomic weights (or equivalents) of chemically analogous elements are merely accidental. We must, however, leave to the future the discovery of the lawfulness which appears in these figures".[83]

M. Carey Lea published a two-part paper in 1860 (pre-Karlsruhe) on relationships between the "equivalents" of the elements,[84] using the values for the latter given in Kopp and Will's Jahresbericht for 1857 (publ. August 1858). He acknowledged the earlier work of Cooke in this field. In this paper Carey Lea noted that many of the previously-accepted relationships no longer held for the more accurate 1857 "equivalents", but claimed that there nevertheless still existed various simple and significant relationships. He remarked on the frequency with which the number 44 or 45 occurs in sum and difference relationships, and pointed out that even more occurrences of these numbers become apparent if we extend the concept of "equivalent" to include negative values. For example, in the group N, P, As, Sb, the differences Sb-As and As-P are 45 and 44 respectively, but P-N is only 17; however, if we use -14 instead of +14 as the "equivalent" of N, then the difference P-N becomes 31-(-14) = 45. If 44 or 45 is subtracted several times from this figure of -14, the results frequently represent the "equivalents", or integral multiples of the "equivalents", of the elements of the nitrogen group (and also, in fact, of elements which bear little resemblance to N, P, As and Sb, such as Sn and Pb). On the basis of the series obtained by such successive subtraction of 44 or 45 from -14, and the corresponding positive series P=31, As=75, Sb=120.3, -=164, Bi=208,

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[81] O sovremennom napravlenii khimii, Gornyi Zhurnal, 1859, no. 1, pp. 103-23; no. 2, pp. 321-35; no. 3, pp. 564-89. (See PLSM, 449-50).

[82] Theorien und Exporimente zur Bestimmung der Atomgewichte der Elemente, 1859.

[83] Ibid., p.146.

[84] On Numerical Relations existing between the Equivalent Numbers of Elementary Bodies, Amer. J. Sci. [2], 29 (May 1860) 98-111, 349-60.

Carey Lea predicted the existence of an element of "equivalent" 164.[85] A second prediction by Carey Lea was that of an analogue of Ag and Au with an "equivalent" of about 152.5,[86] on the basis of the series -

44.5{	197	Au = 197
	152.5	- = -
44.5{	108	Ag = 108
44.5{	63.5	Cu = 63.4

Many other relationships involving the numbers 44 and 45 were pointed out by Carey Lea, e.g. the fact that for the group B(11), C(12) and Si(21) the sum of the "equivalents" = 44. He noted also that many pairs of "equivalents" are in the same ratio as O:N (4:7) or C:N (3:7). He suggested that V be included in the nitrogen group, acknowledging the similar view of Schafarik.[87]

In 1862 Carey Lea published a paper in which he defended himself against criticisms which had been made concerning his introduction of negative "equivalents". He stated that his use of such numbers was merely a mathematical technique for demonstrating otherwise hidden relationships, and of course did not signify masses "less than nothing".[88]

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[85] An element with such an atomic-weight value was in fact subsequently discovered, viz. Ho = 164.9; but this is a rare-earth element, not an analogue of Sb and Bi.

[86] The rare-earth element Eu (discovered 1900) has an atomic weight of 152.

[87] A. Schafarik, Sitzungsbericht of the Acad. of Sciences, Vienna, 33 (1858) 3.

[88] Amer. J. Sci. [2], 34 (1862) 387.

C. The era of discovery of the periodic law: 1862-1871.

1. A.E.B. de Chancourtois: 1862 and 1863

De Chancourtois was a mineralogist and geologist, not a chemist. He seems to have been a systematist by nature.[89] His work on the systematisation of the chemical elements was prompted by a desire to find a classificatory system of the elements which could serve as a basis for his lithological studies; this search led him to a 3-dimensional classification in which the elements (and also certain compound radicals) are arranged according to their characteristic weights along a helical curve inscribed on the surface of a cylinder:[90]

> Geological studies in the field of research opened up by M. Elie de Beaumont in his note on volcanic metalliferous intrusions (émanations)[91] have led me, for the completion of a lithological memoir on which I am now engaged, to a natural classification of the simple bodies and radicles by a table in the form of a helix, founded on the use of numbers which I call characteristic numbers or numerical characteristics.[92]

De Chancourtois had not attended the Karlsruhe Congress, nor does he seem to refer to Cannizzaro by name. Nevertheless, in the case of most elements his "characteristic numbers" correspond closely to the atomic weights of Cannizzaro.[93] De Chancourtois himself had the following to say about his "characteristic numbers":

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[89] See Spronsen, Bibl.110, p.97.

[90] The results of de Chancourtois' work in this field were contained in two memoirs submitted to the French Academy of Sciences in April 1862 and March 1863. Extracts from these memoirs, and additional notes relating to the subject, were published in Comptes Rendus, 1862 (54, pp. 757, 840, 967; 55, p.60), 1863 (56, pp. 253, 479), and 1866 (63, p.24). Because of technical difficulties, the Comptes Rendus did not publish the charts which had accompanied de Chancourtois' reports. De Chancourtois therefore published independently a pamphlet containing most of what had already been published in the Comptes Rendus, together with the graphical representations of his system: Vis Tellurique: Classement naturel des corps simples ou radicaux, obtenu au moyen d'un système de classification hélicoïdal et numérique, Paris, 1863.

[91] Elie de Beaumont, Bull. Soc. Geol. France [2], 4 (1847) 1249.

[92] Extract from de Chancourtois' first memoir (1862), translated by P.J. Hartog in a paper entitled A first foreshadowing of the periodic law, Nature, 41 (Dec. 1889) 186-8; p.186.

[93] Some exceptions were: V, 69 (Cann.), 137-140 (de Ch.); Zr, 90 (Cann.), 67 (de Ch.); Tl, 204 (Cann.), 103 (de Ch.).

> My [characteristic] numbers, which are immediately deduced from the measure of the equivalents or other physical or chemical capacities of the different bodies, are, in the main, the proportional numbers given by the treatises on chemistry, these being reduced to half in the case of hydrogen, nitrogen, fluorine, chlorine, bromine, iodine, phosphorus, arsenic, lithium, potassium, sodium, and silver; in other words, I either divide the equivalents of these bodies by two in the system in which oxygen is taken as 100, or multiply by two the equivalents of the other bodies in the system in which hydrogen is taken as unity.[94]

De Chancourtois used only whole numbers for his "characteristic numbers", in accordance with Prout's commensurability hypothesis, PCH(1; H=1).[95] Apart from Prout, his only predecessor in the study of atomic-weight relationships to whom de Chancourtois refers by name is Dumas.[96]

In his classificatory system, which de Chancourtois called the vis tellurique ("telluric screw"), a spiral (helix) is inscribed upon the surface of a vertical cylinder, making a 45° angle with the base of the cylinder. Taking as the unit of length $\frac{1}{16}$ of a 360° turn of the helix, the "characteristic points" of the elements and radicals are then marked off along the helix at distances corresponding to their "characteristic numbers" based upon H = 1. Nearly all the elements known at the time were included by de Chancourtois in his system.[97]

As de Chancourtois himself pointed out, his vis tellurique can easily be represented in 2-dimensional form "by supposing the surface of the cylinder developed" on a plane surface. A simplified version of the upper part of de Chancourtois' system, "developed" onto a plane in this way, is given below (Fig. III-1).[98]

De Chancourtois summarised the merits of his helicoidal system in the following words:

> ... by its aid I am enabled to enounce the fundamental theorem of my system: The relations between the properties of different bodies are manifested by simple geometrical relations between the positions of their characteristic points.

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[94] See Hartog, op.cit., p.186.

[95] See earlier, pp.63-4.

[96] See Hartog, op. cit., p.186.

[97] According to Spronsen, Bibl.110, p.55, de Chancourtois' system listed 57 of the 63 elements known at the time; but see n.101 below.

[98] Fig. III-1 is based upon the figure given by Hartog, op.cit., p.187.

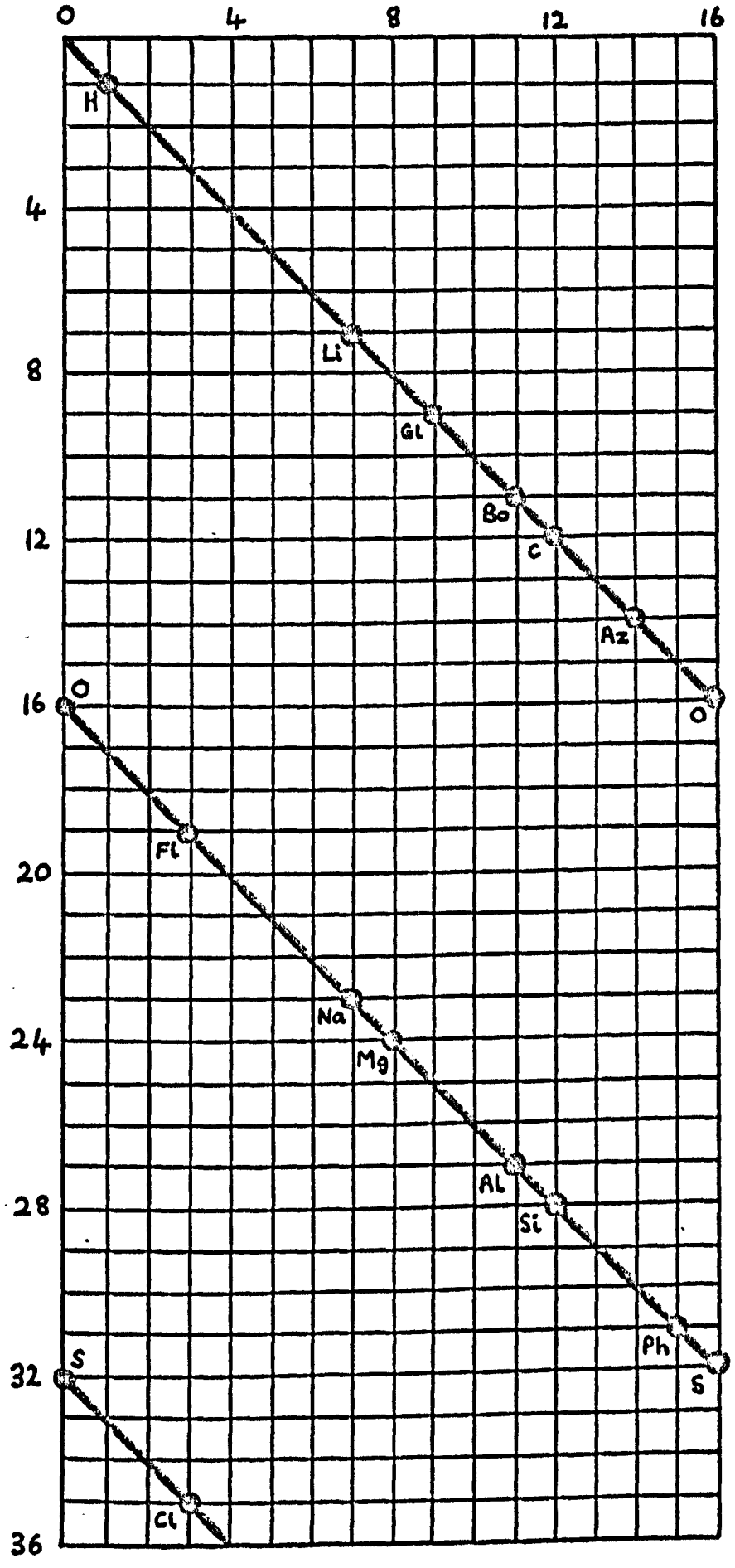

Fig.III-1 (de Chancourtois, 1862).

> ... as a complement to the first theorem we may add the following: Each helix drawn through two characteristic points and passing through several other points or only near them, brings out relations of a certain kind between their properties; likenesses and differences being manifested by a certain numerical order in their succession, for example, immediate sequence or alternation at various periods.[99]

To illustrate his "fundamental theorem" de Chancourtois gave the following examples:

> For instance, oxygen, sulphur, selenium, tellurium, bismuth, fall approximately on the same generating line,[100] while magnesium, calcium, iron, strontium, uranium and barium, fall on the opposite generating line. On either side of the first of these lines we find hydrogen and zinc on the one hand, bromine and iodine, copper and lead on the other; parallel to the second line we find lithium, sodium, potassium, manganese, etc.[101]

Certain elements in de Chancourtois' system were classified not only according to their usual "characteristic numbers", but also according to so-called "secondary characteristics", e.g. in addition to C=12 de Chancourtois included also the "secondary characteristic" C=44, largely on the basis of a consideration of the specific-heat value of diamond from the point of view of the law of Dulong and Petit.

De Chancourtois drew attention to what he considered to be an important parallel between the nature of the chemical elements and the nature of numbers. In his first communication to the Paris Academy he wrote:

> ... I have been led to conceive the possibility of reproducing the series of natural numbers in the series formed by the numerical characteristics of the real or supposed simple bodies supplemented by the characteristics of the compound radicles formed from Gazolytic [sc. non-metallic] elements, such as cyanogen, the ammoniums, etc., and doubtless also by the compound radicles formed from metallic elements, of which the alloys offer us an example. In this natural series, the bodies which are really simple, or at least irreducible by the ordinary means at our disposal, would be represented by the prime numbers. It will be at once seen that there are in my table at least twelve bodies, which, like sodium (23), have characteristics which are prime numbers ... I believe ... that there is a perfect agreement between bodies, the elements of the material order, and numbers, the elements of the abstract order of things (éléments de la variété matérielle, de la variété abstraite).[102]

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[99] See Hartog, op.cit., p.186.

[100] Hartog and Spronsen both claim that the inclusion of Bi here is probably a misprint, because it is not on the same generator as O, S, Se and Te. However, it is "approximately" on the same generator, viz. on an adjacent one.

[101] See Hartog, op.cit., p.186. According to Spronsen, Ba and Pb are absent from de Chancourtois' vis tellurique; however, this passage suggests that they are included. I have been unable to see de Chancourtois' pamphlet of 1863 in order to check this point.

[102] See Hartog, op.cit., p.187.

In his second communication to the Academy de Chancourtois expressed the "general conclusion", "The properties of bodies are the properties of numbers."[103]

Very little attention was paid to de Chancourtois' work when it was first published, although it was mentioned by Kopp and Will in their Jahresbericht of 1862 and 1863[104], and referred to by C.J. Sainte-Claire Deville in 1862[105]. Later it was mentioned by Wurtz (1879),[106] Berthelot (1885)[107] and Mendeleev (Faraday Lecture, June 1889);[108] but it was not until Hartog in England (Dec. 1889)[109] and de Boisbandran and de Lapparent in France (1891)[110] claimed a certain priority for de Chancourtois in connection with the discovery of the periodic law that his work gained widespread appreciation.[111]

2. J.A.R. Newlands: 1863-1866

Newlands did not attend the Karlsruhe Congress; he was in Italy at the time, fighting under Garibaldi[112]. He returned to England in November, 1860[113]. He worked in London, as an industrial chemist.

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[103] Ibid., p.188.

[104] Jahresbericht, 15 (1862) 6; 16 (1863) 14.

[105] Comptes rend., 54 (1862) 782.

[106] Bibl. 132.

[107] Les Origines de l'Alchimie, p.302.

[108] See Bibl. 47, p.326; PLBA, 213.

[109] Op.cit.

[110] Comptes rend., 112 (1891) 77; Chem. News, 63 (1891) 51.

[111] The reasons for the initial lack of appreciation of de Chancourtois' work are discussed later, in Ch. VIII, where an attempt at an objective appraisal of his contribution is also given. (In general, questions which go beyond the mere factual account of the contributions of various scientists towards the emergence of the periodic system - such as questions of the merits and defects of these contributions, of the degree of impact upon the scientific community, and of priority - are considered in Ch. VIII rather than in the present chapter.)

[112] Newlands' mother was of Italian descent.

[113] See W.H. Taylor, Bibl. 112.

In 1862 Newlands published a paper which included a system for classifying organic substances.[114] In 1863, still in ignorance of Cannizzaro's work, and unaware of de Chancourtois' contribution, Newlands published his first attempt at classifying the chemical elements.[115] This classification, which arranged the elements into eleven families, was somewhat reminiscent of Odling's contribution of 1857[106]; but unlike Odling in 1857, and certain other contributors of the 1850's (particularly Cooke, Dumas and Mercer), Newlands in 1863 had still not reached the stage of investigating relationships between the different groups of elements. On the other hand, Newlands in 1863 showed a greater tendency than had most of his predecessors for the specific prediction of unknown elements on the basis of his system: thus, he predicted the existence of a new alkali metal of atomic weight 163, and mentioned the possibility of the existence of an element which could serve as the middle member of a triad of which Rh (52.2) and Ir (99) are the extremes.[117]

The second stage in the development of Newlands' attempts at classifying the elements came in July 1864, when he used the new atomic weights (determined according to the views of Cannizzaro) given by Williamson.[118] Acknowledging its incompleteness, and mentioning that he had prepared other tables "of a more complete character", Newlands presented a system of 37 elements arranged in 10 horizontal families[119] (see Fig. III-2, below). This arrangement corresponds more or less to the order of increasing atomic weight, although Te and I are in the inverse order, and the sequence is broken also by the groups IX and X, and by Bi in the last column. Newlands left many blank spaces, including those appropriate for Al, Sc, Y, In and Ge. For the space corresponding to Ge he predicted an element of atomic weight 73, from the triad-relationship, $\frac{Si(28) + Sn(118)}{2} = 73$ (the modern value for Ge, referred to H=1, is 72.0). Near the end of his article of July 1864 Newlands wrote: "So frequently

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[114] J. Chem. Soc., 15 (1862) 36.

[115] On Relations among the Equivalents, Chem. News, 7 (1863) 70-72; p.71. (Given in Bibl.110, p.104; Bibl.47, p.260).

[116] Newlands does not mention Odling in his 1863 paper; of his predecessors he mentions only Dumas by name (op.cit., p.70).

[117] These predictions have not been confirmed.

[118] A.W. Williamson, On the classification of the elements in relation to their atomicities, J.Chem. Soc. [2], 17 (1864) 211-222.

[119] Relations between equivalents, Chem. News, 10 (1864, July 30) 59-60; p.59.

			triad			
			lowest term	mean	highest term	
I		Li 7	+17 = Mg 24	Zn 65	Cd 112	
II		B 11				Au196
III		C 12	+16 = Si 28		Sn 118	
IV		N 14	+17 = P 31	As 75	Sb 122	+88 = Bi210
V		O 16	+16 = S 32	Se 79.5	Te 129	+70 = Os199
VI		F 19	+16.5= Cl35.5	Br 80	I 127	
VII	Li 7	+16 = Na 23	+16 = K 39	Rb 85	Cs 133	+70 = Tl203
VIII	Li 7	+17 = Mg 24	+16 = Ca 40	Sr 87.5	Ba 137	+70 = Pb207
IX			Mo 96	V 137	W 184	
X			Pd106.5		Pt 197	

Fig. III - 2 (Newlands, July 1864).

	no.		no.		no.		no.		no.	
Group a	N	6	P	13	As	26	Sb	40	Bi	54
b	O	7	S	14	Se	27	Te	42	Os	50
c	Fl	8	Cl	15	Br	28	I	41	-	-
d	Na	9	K	16	Rb	29	Cs	43	Tl	52
e	Mg	10	Ca	17	Sr	30	Ba	44	Pb	53

Fig. III - 3 (Newlands, Aug. 1864).

No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co&Ni 22	Br 29	Pd 36	I 42	Pt&Ir 50
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 53
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Cd*38	Ba&V 45	Pb 54
Bo 4	Al 11	Cr 19	Y 24	Ce&La 33	U 40	Ta 46	Th 56
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52
N 6	P 13	Mn 20	As 27	Di&Mo 34	Sb 41	Nb 48	Bi 55
O 7	S 14	Fe 21	Se 28	Ro&Ru 35	Te 43	Au 49	Os 51

(*Original has misprint "Bd" here).
Fig.III-4 (Newlands, 1865).

No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co&Ni 22	Br 29	Pd 36	I 42	Pt&Ir 50
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Os 51
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Cd 38	Ba&V 45	Hg 52
Bo 4	Al 11	Cr 19	Y 24	Ce&La 33	U 40	Ta 46	Tl 53
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Pb 54
N 6	P 13	Mn 20	As 27	Di&Mo 34	Sb 41	Nb 48	Bi 55
O 7	S 14	Fe 21	Se 28	Ro&Ru 35	Te 43	Au 49	Th 56

Fig.III-5 (Newlands, 1866).

are relations to be met with among the equivalents of allied elements, that we may almost predict that the next equivalent determined, that of indium, for instance, will be found to bear a simple relation to those of the group to which it will be assigned".[120]

Within a month Newlands had published another (partial) table, in which he included neither atomic-weight values nor atomic-weight differences, but characterised the elements instead by means of their "ordinal numbers" when arranged according to increasing atomic weight[121] (see Fig. III-3). He pointed to the following relationship: "calling hydrogen 1, lithium 2, glucinium 3, boron 4, and so on (a separate number being attached to each element having a distinct equivalent of its own, and where two elements happen to have the same equivalent, both being designated by the same number)... the eighth element starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music".[122]

A year later, in August 1865, Newlands published a table of 62 elements arranged in 8 vertical columns, and forming 7 horizontal families[123] (see Fig. III-4). This table unlike his earlier systems, contained no blank spaces for any elements which had yet to be discovered. In the announcement accompanying this table of 1865 Newlands wrote:

> If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table,

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[120] Ibid., p.60. Although Newlands had adopted Cannizzaro's atomic-weight values, he tended to refer to these values as "equivalents". Later in 1864 Newlands published two papers on the atomic weight and family-membership of indium, entitled Equivalent of indium (Chem. News, 10, Aug. 20, p.95) and On the equivalent of indium (ibid., Nov. 12, p.240). In the first of these papers he suggested that the atomic weight of indium "may prove to be identical, or nearly so, with those of zinc or cadmium", on the grounds of the chemical analogy to zinc claimed for indium by Roscoe. In the second paper he took the atomic-weight value In = 74.14; he suggested that indium may be an analogue of Si and Sn, or of Al and U, or of Zn, concluding that, "We must, however, wait for further details of the properties of this newly discovered element, and especially of its atomicity, before it can be safely assigned to any particular group".

[121] On relations among the equivalents, Chem. News, 10 (1864, Aug. 20) 94.

[122] Ibid.

[123] On the law of octaves, Chem. News, 12 (1865, Aug. 18) 83. By this time Odling had published his first "periodic" system (in Oct. 1864 - see below).

it will be observed that elements belonging to the same group usually appear on the same horizontal line.

[Table]

It will also be seen that the numbers [sc. "ordinal numbers"] of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also.

This peculiar relationship I propose to provisionally term the "Law of Octaves".[124]

A week after this enunciation of his "law of octaves" Newlands published another short article, in which he claimed that "all the numerical relationships among the equivalents, pointed out by M. Dumas and others, including the well-known triads, are merely arithmetical results flowing from the existence of the 'Law of Octaves'".[125]

On March 1st, 1866, Newlands presented his ideas on the "law of octaves" at a meeting of the Chemical Society, asserting his claim to the discovery of the law.[126] This paper was not published in the Society's Journal,[127] but its contents and reception were reported a week after the meeting in the Chemical News.[128] The table which accompanied the report in the Chemical News, and which had been shown at the meeting of the Chemical Society, resembled the one of 1865, but the cases of discontinuity in the series of ordinal numbers had been greatly reduced (see Fig. III-5). Like his 1865 table, Newlands' table of 1866 lacked blank spaces for possible unknown elements. At the Chemical Society meeting Gladstone had objected

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[124] Ibid.

[125] On the cause of numerical relations among the equivalents, Chem. News, 12 (1865, Aug. 25) 94.

[126] Newlands' priority in this respect had not been challenged; however, he was by now undoubtedly aware of Odling's related work on the classification of the elements.

[127] Newlands' paper was returned to him as "not adapted for publication in the Society's Journal" (see Taylor, Bibl.112). When in 1873 Newlands asked Odling (then President of the Society) why his 1866 paper had been turned down, Odling is reported to have replied that it was because the Society "had made it a rule not to publish papers of a purely theoretical nature, since it was likely to lead to correspondence of a controversial character" (Chem. News, 27, 1873, p.318).[128]

[128] Chem. News, 13 (1866, March 9) 113.

to this latter feature of Newlands' system, pointing out that four new elements had been discovered during recent years (Cs, 1860; Rb, Tl, 1861; In, 1863). Gladstone had also remarked that the elements in the last column of Newlands' table seemed to resemble each other more than they did the other elements of the horizontal families in which they had been placed. Any reply given by Newlands at the meeting to the "no blank space" objection is not on record; to Gladstone's second objection Newlands replied that the metals in the final column resemble both each other and the corresponding elements in the horizontal series. Also at the meeting, George Carey Foster "humorously inquired of Mr. Newlands whether he had ever examined the elements according to the order of their initial letters".[129] Foster believed that a system such as Newlands' could result from coincidence, and criticised what he considered to be the unsatisfactory separation of Fe from Co and Ni, and of Mn from Cr. Newlands replied to Foster that he had tried other arrangements, but that the classification based upon ordering the elements according to Cannizzaro's atomic weights had given the best results.

On 16th March 1866 a paper by Newlands was published in the Chemical News, containing the following reply to Gladstone's "no blank space" criticism of his table: "for, although the difference in the [ordinal] numbers of analogous elements might in that case [sc. the case of the discovery of new elements] be altered from 7, or a multiple of 7, to 8, 9, 10, 20, or any conceivable figure, the existence of a simple relation among the numbers of analogous elements would be none the less evident".[130] This reasoning assumes that any newly-discovered elements would belong to one or more new chemical families.[131] In the same paper Newlands expressed his "law of octaves" as: "The numbers of analogous elements, when not consecutive, differ by 7, or by some multiple of 7".[132]

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[129] Ibid.

[130] On the "Law of Octaves", Chem. News, 13 (1866, March 16) 130.

[131] Unlikely though such an assumption may have been, it was in fact partly substantiated by the discovery of the inert gases.

[132] Op.cit. Newlands went on to comment on the difference in wording of this form of expression of his "law of octaves" from that which he had given in 1865: "The clause 'when not consecutive' was introduced for the purpose of embracing certain analogous elements whose atomic weights are consecutive, e.g. the series containing chromium No. 19, manganese No. 20, iron No. 21, nickel and cobalt No. 22, copper No. 23, and zinc No. 24". It was apparently in this modified form that Newlands expressed his "law of octaves" at the meeting of the Chemical Society on 1st March 1866.

Newlands' "law of octaves" and his classificatory system based upon it did not achieve general recognition by the scientific community of the time. He later re-published his various papers of the 1860's and 1870's on atomic-weight relationships and the classification of the elements as a single collection in a book of 1884 (Bibl. 84) in which he claimed priority of discovery of the periodic law (as his "law of octaves").

3. W. Odling: 1864 and 1865

Odling had long supported the unitary ideas of Laurent and Gerhardt. In 1860 he had attended the Karlsruhe Congress, where he had read a paper emphasising that an element cannot have more than one atomic weight. He did not, however, immediately accept the views expressed at the Congress by Cannizzaro; thus, in 1863 he wrote -

> ... in the great majority of instances, the molecules we have deduced from chemical considerations, are identical with the molecules deduced from the physical law of gaseous volumes enunciated by Ampère, namely, that all gases contain the same number of molecules within the same volume ... some chemists attach so great an importance to the law of volumes, that they would be guided exclusively by it, and would accord to all bodies whatsoever, such atomic weights as would be in accordance with it. In the present state of knowledge, however, it seems to us preferable to deduce the chemical atom or molecule of a body chiefly from chemical considerations ...
>
> It is evident that the atomic weights proposed by Cannizzaro, from considerations of specific heat, frequently correspond with those which he and others have been led to from considerations of atomic volume ... Cannizzaro's proposal ... would involve the dissassociation [sic] of silver from lead, and that of the metals of the alkalis from those of the alkaline earths. The chlorides of silver and potassium, for instance, would be represented as protochlorides by the formulae AgCl and KCl respectively, whilst those of lead and barium would be represented as dichlorides by the formulae $PbCl_2$ and $BaCl_2$ respectively. Now the highly basic characters of the alkaline earth-metals, the strongly alkaline reactions of their dissolved hydrates, the perfect neutrality and great permanency of their salts, seem to demonstrate their analogy to undisputed protoequivalent metals, such as potassium, rather than to undisputed di-equivalent metals, such as tin ...
>
> It seems to us that the objections to Cannizzaro's general proposition, are, in the present state of knowledge, too great to admit of its adoption.[133]

By October 1864, however, Odling had come to accept Cannizzaro's views,[134] publishing at this time a paper containing a classificatory system of the elements (see below, Fig. III-6) based upon Cannizzaro's

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[133] Bibl.129, vol. I, 1863, pp.466-71: from an article by Odling on Atomic weights, pp.452-73.

[134] Odling did use the old, pre-Cannizzaro, atomic-weight values in a publication of 1865, although solely on grounds of expediency, not because he considered them superior to Cannizzaro's values (see below).

atomic weights.[135] As in the case of Newlands, Odling's conversion to Cannizzaro's atomic-weight system seems to have been influenced by Williamson.[136] Odling's classificatory work of 1864 appears to have been carried out quite independently of Newlands' related work.

In his paper of October 1864 Odling pointed to various atomic-weight relationships. He noted particularly the common occurrence of atomic-weight differences of 84.5 to 97, of ½(84.5 to 97) and of 16 between analogous elements. Referring to those pairs of analogous elements with atomic-weight differences in the range 84.5 to 97, such as I-Cl, Au-Ag, Cs-K, Bi-Sb, he commented, "In about one-half of the above instances, the two elements associated with one another are known to be the first and third terms respectively of certain triplet families; and the discovery of intermediate elements in the case of some or all of the other pairs, is not by any means improbable."[137] In the case of pairs such as I-Br, Sn-Mg, with atomic-weight differences of about ½(84.5 to 97), he considered that "there seems no reason to anticipate the existence of an intermediate term".[138] It seems likely that the spaces marked " in Odling's main classificatory system in this paper (Fig. III-6) were intended to represent possible unknown elements, although he does not state this explicitly. Later in the paper he lists as an analogue of Au 196.5 and Ag 108 an element X63, which does indeed correspond to one of the spaces marked " in his main system (he places Cu 63.5 elsewhere in the system).

One of the most important of Odling's contributions in his 1864 paper was his recognition of sub-groups within groups of analogous elements. He related the existence of sub-groups to the particular values of the atomic-weight differences within a group, pointing out that the elements within a given sub-group tend to have atomic-weight differences of about 48. He presented a table showing the separation of the groups into sub-groups, e.g.

	"	"	Ag 108		Au 196.5
L7	Na 23	"	"		Tl 203
	K 39	Rb 85	Cs 133		"

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[135] On the proportional numbers of the elements, Quarterly Journal of Science, 1 (1864) 642-8. Odling's classificatory system is on p.643 of this paper.

[136] See Spronsen, Bibl.110, p.113.

[137] Op.cit., p.644

[138] Ibid.

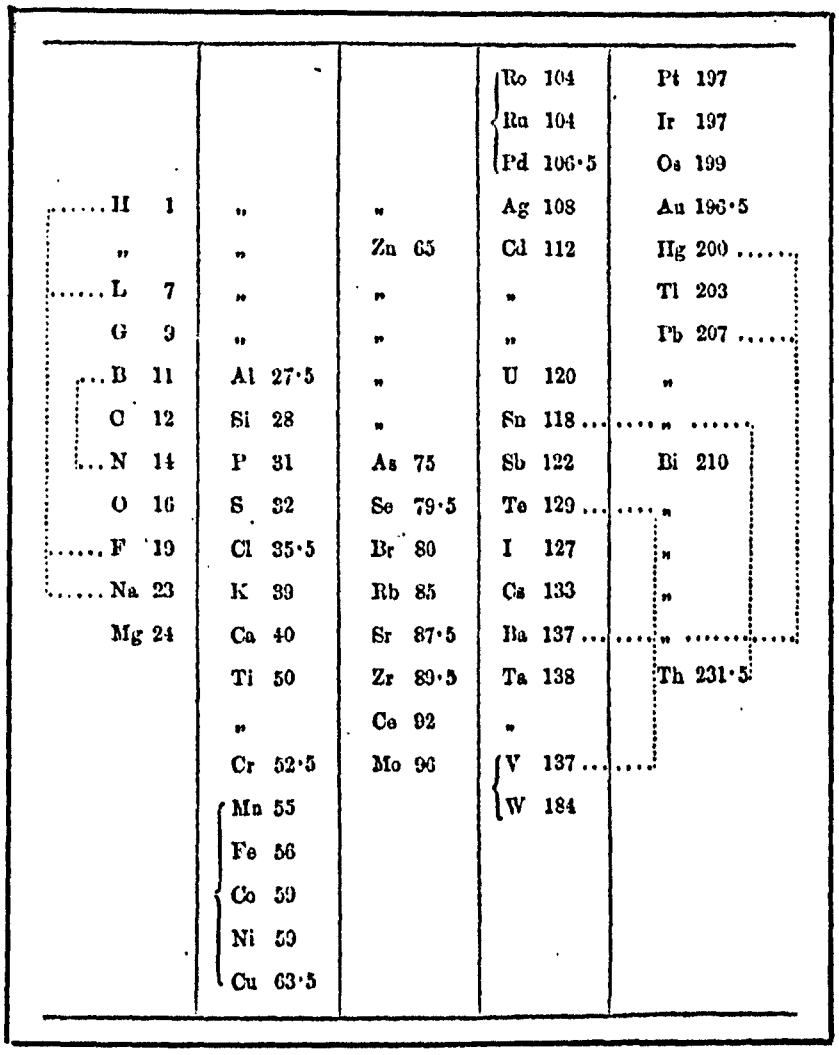

Fig.III-6 (Odling, 1864).

			~~Mo~~ 96	~~W~~ 184
			-	Au 196.5
			~~Pd~~ 106.5	~~Pt~~ 197
L 7	Na 23	-	Ag 108	-
~~G~~ 9	~~Mg~~ 24	~~Zr~~ 65	~~Cd~~ 112	~~Hg~~ 200
B 11	~~Al~~ 27.5	-	-	Tl 203
C 12	Si 28	-	Sn 118	~~Pb~~ 207
N 14	P 31	As 75	Sb 122	Bi 210
O 16	S 32	Se 79.5	Te 129	-
F 19	Cl 35.5	Br 80	I 127	-
	K 39	Rb 85	Cs 133	-
	~~Ca~~ 40	~~Sr~~ 87.5	~~Ba~~ 137	-
	Ti 48	Zr 89.5	-	Th 231
	~~Cr~~ 52.5	-	~~V~~ 138	-
	~~Mn~~ 55 etc.			

Fig.III-7 (Odling, 1865: Watts' Dictionary).

	Triplet Groups			
			Mo 96	W 184
H 1			-	Au 196.5
			Pd 106.5	Pt 197
Li 7	Na 23	-	Ag 108	-
G 9	Mg 24	Zn 65	Cd 112	Hg 200
B 11	Al 27.5	-	-	Tl 203
C 12	Si 28	-	Sn 118	Pb 207
N 14	P 31	As 75	Sb 122	Bi 210
O 16	S 32	Se 79.5	Te 129	
F 19	Cl 35.5	Br 80	I 127	
	K 39	Rb 85	Cs 133	
	Ca 40	Sr 87.5	Ba 137	
	Ti 48	Zr 89.5	-	
	Cr 52.5	-	V 138	
	Mn 55 etc.	-		

Fig.III-8 (Odling, 1865: Course of Practical Chemistry).

Odling concluded this paper with the remark: "Doubtless some of the arithmetical relations exemplified in the foregoing tables and remarks are simply accidental; but taken altogether, they are too numerous and decided not to depend upon some hitherto unrecognised general law".[139]

In 1865 a classificatory system of the elements by Odling was published in Watts' Dictionary of Chemistry[140] (see Fig. III-7). Pointing out that in this table he was "allowing chromium and manganese to stand proxy for the iron metals, and palladium and platinum for their respective congeners", Odling described the table as being "slightly modified" from the one he had published in 1864. He summarised briefly his main observations and conclusions of 1864.

A similar table (Fig. III-8) was published shortly afterwards in an appendix to the 2nd edition (1865) of Odling's A course of Practical Chemistry arranged for the use of medical students.[141] This table was entitled "Atomic Weights and Symbols". No accompanying explanation or comment was given; but in the preface to the book (dated June, 1865) Odling wrote - "To maintain its adaptability to the wants of the medical student, the old scale of atomic weights has been exclusively employed throughout the body of the work. In a short Appendix, however, some tables have been set up, in which the new atomic weights are used, with a view to illustrate the superior simplicity and mutual association of the modern unitary over the older dualistic formulae".[142]

The table given by Odling in the 2nd edition of A course of Practical Chemistry is not to be found in the 4th (1869) edition of this work;[143] nor is such a table to be found in his Outlines of Chemistry, 1870, where Odling classifies the elements into various groups solely on the grounds of their usual valency.

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[139] Ibid., p.648.

[140] Bibl.129, vol.III, 1865, p.975: in a section by Odling entitled Metals, atomic weights and classification of, pp.975-6.

[141] Bibl.86, p.226.

[142] Ibid., pp.v-vi.

[143] Spronsen (Bibl.110, p.115) presents a table very like those given in Figs. III-7 and III-8, which he claims is from A course of Practical Chemistry, 3rd edn., 1868, p.226; but there are certain indications that this is a mistaken reference, and should in fact be to the 2nd edn., 1865. I have been unable to see a copy of the 3rd edn. in order to check Spronsen's reference.

Odling's classificatory work of the 1860's received very little attention. In 1871 an attempt was made by Gerstl (the London correspondent of Berichte) to contend priority on Odling's behalf in connection with the construction of the periodic system[144], but the small response which this attracted was transient and dismissive[145]. By the end of the 19th century Odling's classificatory work of the 1860's seems to have been almost forgotten, unlike the cases of de Chancourtois and Newlands whose contributions of the 1860's had by this time gained fairly general acknowledgment.

4. G.D. Hinrichs: 1864-1869

Hinrichs studied in Denmark until 1861, when he left the University of Copenhagen for the U.S.A. He had not attended the Karlsruhe Congress. In 1862 he joined the University of Iowa. By 1866 he was apparently familiar with the work of Cooke, Dumas and Carey Lea on atomic-weight relationships and the classification of the elements.[146] He seems to have followed the Comptes Rendus with great interest, and had published a number of papers in it[147], but whether he knew of de Chancourtois' work is not known; he does not mention de Chancourtois.

In 1864 Hinrichs published two papers on astronomy[148], the second of which opened with the words, "As soon as I heard of the great discovery of Kirchhoff and Bunsen sc. spectroscopic analysis, 1859-60 , I felt sure that the dark lines of the elements would prove to be distributed according to simple laws, and that these laws might lead us to a knowledge of the relative dimensions of the atoms."[149] In 1866 he published a paper in which he said, "Believing the scientific public now more apt [sc. because of the recent spectral data, especially those obtained by J. Plücker] to give a hearing to our theory, we intend to publish a series of articles, giving the properties of the chemical elements as functions of their atomic weights".[150] In this paper Hinrichs classified the elements into groups, giving a formula

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[144] Berichte, 4 (1871) 132, 484.

[145] An example of such a reaction was that of Mendeleev, in his paper Zur Frage über das System der Elemente, Berichte, 4 (1871) 348-52 (see Ch. VIII).

[146] According to Spronsen, Bibl.110, p.116.

[147] See Zapffe, Bibl. 135.

[148] Amer. J. Sci. Arts [2], 37 (1864) 36; 38 (1864) 420-1.

[149] Ibid., p.420.

[150] Ibid., 42 (1866) 350-68.

for the atomic weights of the elements of each group, e.g. for the group O(16), S(32) Se(80) and Te(128) he gave the formula $A=n4^2$, where n=1, 2, 5 and 8 respectively. Hinrichs took the correlations between his characteristic formulae for the different groups to reflect fundamental correlations between the groups. Also, he showed that the product nxd (where d is the interval of the dark spectral lines) is almost constant for a given group. At the base of Hinrichs' considerations in this paper was a belief in the existence of a single primary substance whose atoms had a weight $\frac{1}{4}$H.

In 1867 was published a lithographed reproduction of a manuscript book by Hinrichs entitled Programm der Atomechanik oder die Chemie eine Mechanik der Panatome,[151] which, according to Hinrichs, had been written as early as 1855.[152] This book contained a circular, or radial, classificatory system of the elements, a simplified version of which is given below (Fig.III-9).[153] In his Atomechanik Hinrichs assumed a primary substance, or "pantogen", of atomic weight $\frac{1}{2}$H, expressing the atomic weights of the chemical elements as multiples of the "panatom" (e.g. Cl=71). He called these doubled atomic weights "atograms" or "Hinrichs' atomic numbers". In his classification two orders of elements were distinguished, "Trigonoïde" (non-metals) and "Tetragonoïde" (metals): in the former the atoms were considered to contain triangular arrangements of panatoms, and in the latter to contain square arrangements. Hinrichs' circular arrangement is not entirely according to increasing atomic weight (apart from the Te-I question), e.g. strict

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[151] Lithography by Augustus Hagebocck, Davenport, Iowa; publ. from Iowa City, 1867.

[152] See Zapffe, Bibl.135. There were certain entries in the Atomechanik which were coded, and which according to Hinrichs (although he did not explain the code) included the date "February 1855". However, the atomic-weight values used in the Atomechanik are evidently based upon the clarified concept of atomic weight given by Cannizzaro, 1858-60.

[153] Zapffe, Bibl.135, p.468, has written: "The earliest known progenitor of the circular chart as an approach to classification of the elements was in an M.D. thesis presented to the College of Physicians and Surgions of the University of the State of New York, by O.W. Gibbs, 1845 - An Inaugural Dissertation on a Natural System of Chemical Classification (Princeton, NJ - John T. Robinson, 1845)". I have not seen Gibbs' system.

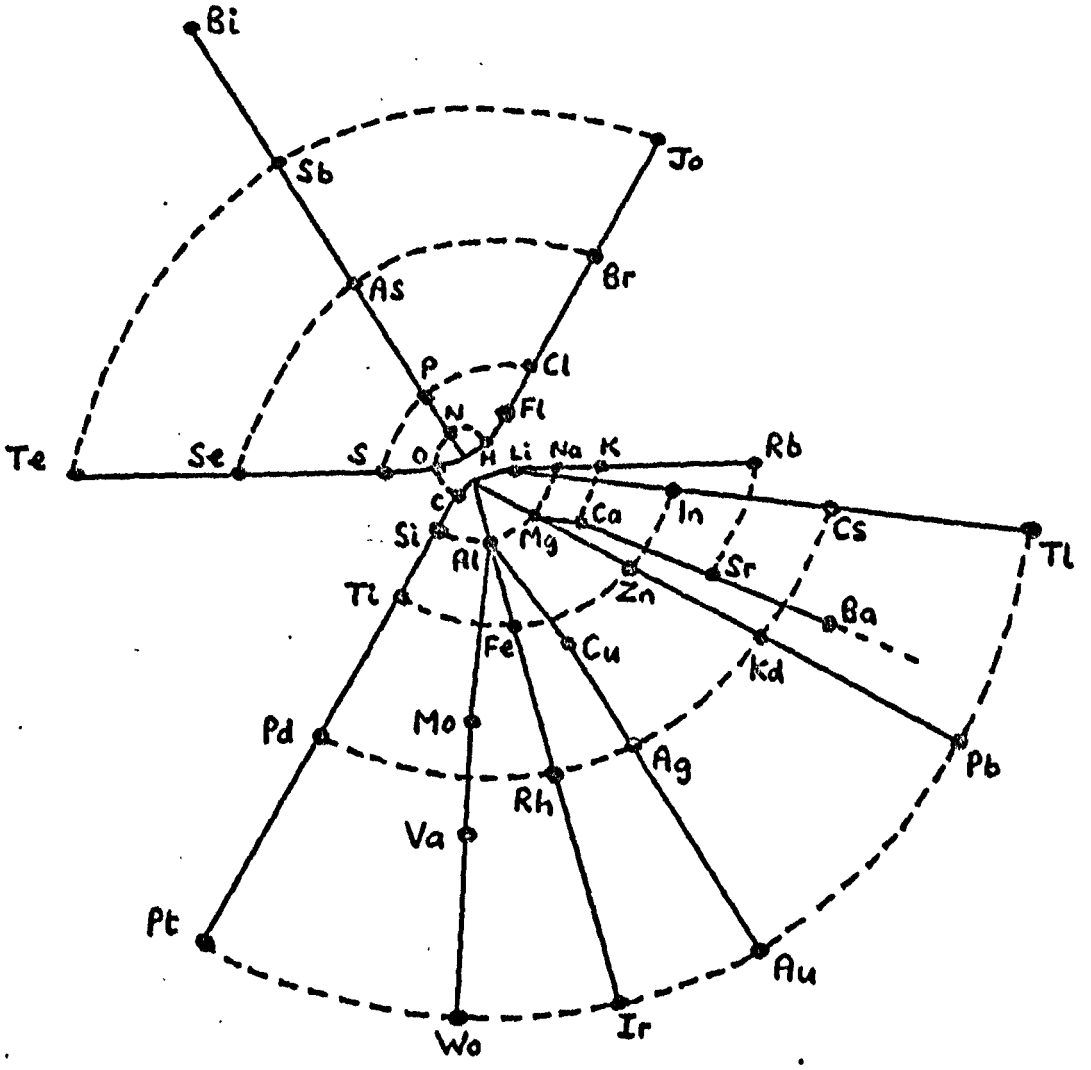

Fig.III-9 (Hinrichs, 1867).

NAME	GROUP	SYMBOL OF THE ELEMENTS							
Pantoïds	Υ	H	-	-	-	-			
Kaloïds	$K\zeta$	Li	Na	Ka	Rb	-			
Chalcoïds	$X\zeta$	-	-	Ca	Sr	Ba			
Cadmoïds	$K\delta$	(Be?)	Mg	Zn	Cd	Pb			
Hydrargoïds	$\Upsilon\gamma$	-	-	-	-	Hg			
Cuproïds	$K\nu$	-	-	Cu	Ag	Au			
Ferroïds	$\Sigma\nu$	(Be?)	Al	Co-Ur Ni Fe	Rh	Ir			
Molybdoïds	$M\lambda$	Bo	-	Mn Cr	Mo	Wo			
Titanoïds	$T\tau$	C	Si	Ti	Pd	Pt			
?					Sn				
Nioboïds	$N\beta$	-	-	Va	Nb	Ta			
Phosphoïds	Φ	N	P	P	As	As	Sb		Bi
Sulphoïds	Θ	O		S	Se	Te			-
Chloroïds	X	Fl		Cl	Br	Io			-
Pantoïds	Υ	H		-	-	-			-

Fig. III-10 (Hinrichs, July 1869).

Genera	Species				
x =	1	2	3	4	5
Υ	H				
$K\alpha$	Li	Na	Ka	Rb	
$X\alpha$	-	-	Ca	Sr	Ba
$K\delta$	-	Mg	Zn	Cd	Pb
$\Upsilon\gamma$	-	-	-	-	Hg
$K\nu$	-	-	Cu	Ag	Au
			Co		
			Ni		
$\Sigma\iota$		Al	Mn	Rh	Ir
			Cr		
$T\tau$	C	Si	Ti	Pd	Pt
				Sn	
Φ	N	P*	As	Sb	Bi
Θ	O	S	Se	Te	-
X	Fl	Cl	Br	Io	-
Υ	H				

(*Original has misprint "T" here).

Fig.III-11 (Hinrichs, autumn 1869).

atomic-weight ordering would require the nitrogen group and the oxygen group to change places. The Atomechanik is concluded with the statement: "The properties of the chemical elements are functions of their atomic weights".

At the 17th meeting of the American Association for the Advancement of Science, in Chicago, August 1868, Hinrichs presented two papers,[154] in the first of which he gave a classification of the elements according to valency and metallic or non-metallic character. At the 18th meeting the following autumn Hinrichs read two more papers.[155] The second of these contained a tabluar classification of the elements (Fig.III-11)[156]; beryllium and boron are absent from this table. In July of the same year Hinrichs had already published a classificatory system in which beryllium and boron had been included (Fig.III-10)[157], although in this system he was undecided about whether beryllium should be placed in the magnesium group or the aluminium group. Hinrichs' table of 1869 contain certain places which have been marked "-"; it is quite probable that these are intended to represent unknown elements, although Hinrichs did not claim this explicitly.

Hinrichs' attempts at classifying the elements had little impact upon the scientific community.

5. J. Lothar Meyer: 1864-1870 (and 1872)

Lothar Meyer had attended the Karlsruhe Congress, 1860. In 1862 he began to write a textbook Die modernen Theorien der Chemie, utilising and developing the ideas of Cannizzaro; this book was published in 1864 (Bibl.80). This first edition of Meyer's Die modernen Theorien contains his first attempt at classifying the chemical elements. Acknowledging the earlier work of Gmelin, Pettenkofer and Dumas in the field, and pointing to the analogy between families of chemical elements and organic homologous series, Meyer classified the elements into two separate tables:

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[154] Proc. Amer. Assoc. Adv. Sci., 17 (1868) 209-223; 223-238.

[155] Ibid., 18 (1869) 100-112; 112-124.

[156] Ibid., p.112.

[157] The Pharmacist (Chicago College of Pharmacy), 2 (July 1869) 10-12; p.12. This table was headed "Hinrichs' classification of the elements", and beneath the table was the comment: "The elements may be considered as species of matter, the groups as genera. The elements Cr, Mn, Fe, Ni, Co-Ur are but varieties, constituting the sub-group of Sideroïds, $\sum\delta$ ".

a main table of 28 elements arranged in 6 families (Fig. III-12a); and a two-part supplementary table, of 6 elements in 2 families, and 16 elements in 5 families (Fig.III-12b).[158] Notable omissions from this classification were the elements boron and aluminium. In the main table an empty space was marked between Si and Sn; Meyer did not comment upon the significance of this space. There is no indication either in the 1864 classification itself or in the accompanying text of any attempt or desire on Meyer's part to unite the separate tables into a single system.

The second classificatory system of the elements drawn up by Lothar Meyer appears to have been a manuscript table dating from 1868, which was prepared for inclusion in the 2nd edition of Die modernen Theorien. However, this 2nd edition was not published until 1872, by which time an improved table was included by Meyer (Fig. III-16: a planar representation of a cylindrical spiral classification). Meyer's 1868 manuscript table was published for the first time in 1895, by Karl Seubert.[159] This table (Fig.III-13) represents an attempt by Meyer to combine his main and supplementary tables of 1864 into a single system. It does not include boron; aluminium is included twice, in both cases out of sequence of increasing atomic weight. It retains the gap marked between Si and Sn in 1864.

Meyer read the German abstract of Mendeleev's first article on the periodicity of properties of the elements, given in Zeitschrift für Chemie, June-July 1869 (see later). In December 1869 he completed his own first article on this subject, which was published in March 1870.[160] This article contained a tabular classificatory system of the elements (Fig.III-14) which Meyer conceded as being "essentially identical to that given by Mendeleev" ("Die nachstehende Tabelle ist im Wesentlichen identisch mit der von Mendelejeff gegebenen").[161] Meyer concluded from his table that "the properties of the elements are largely periodic functions (periodische Functionen) of the atomic weight".[162] Accompanying this same article was

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[158] Bibl.80, 1864, pp.138 and 139. Reprinted in Bibl.67, pp. 4 and 5.

[159] Bibl.67, pp. 6 and 7. Seubert had been a pupil of Meyer's, and subsequently became an assistant and colleague.

[160] Die Natur der chemischen Elemente als Function ihrer Atomgewichte, Annalen (Liebig), Suppl.VII (1870) 354-64. Reprinted in Bibl.67, pp.9-17.

[161] This is a reference to the table by Mendeleev which had been included in the Zeitschrift für Chemie abstract; this table was identical to table 8 (P1) given in Ch.IV of this thesis.

[162] Bibl.67, p.13.

	4-werthig	3-werthig	2-werthig
	—	—	—
Differenz =	—	—	—
	C = 12,0	N = 14,01	O = 16,00
Differenz =	16,5	16,96	16,07
	Si = 28,5	P = 31,0	S = 32,07
Differenz =	89,1/2 = 44,55	44,0	46,7
	—	As = 75,0	Se = 78,8
Differenz =	89,1/2 = 44,55	45,6	49,5
	Sn = 117,6	Sb = 120,6	Te = 128,3
Differenz =	89,4 = 2·44,7	87,4 = 2·43,7	—
	Pb = 207,0	Bi = 208,0	—

	1-werthig	1-werthig	2-werthig
	—	Li = 7,03	(Be = 9,3 ?)
Differenz =	—	16,02	(14,7)
	Fl = 19,0	Na = 23,05	Mg = 24,0
Differenz =	16,46	16,08	16,0
	Cl = 35,46	K = 39,13	Ca = 40,0
Differenz =	44,51	46,3	47,6
	Br = 79,97	Rb = 85,4	Sr = 87,6
Differenz =	46,8	47,6	49,5
	J = 126,8	Cs = 133,0	Ba = 137,1
Differenz =	—	(71 = 2·35,5)	—
	—	(Tl = 204?)	—

Fig.III-12 (a).

	4-werthig	6-werthig
	Ti = 48	Mo = 92
Differenz =	42	42
	Zr = 90	Vd = 137 [3])
Differenz =	47,6	47
	Ta = 137,6 [2])	W = 184

	4-werthig	4-werthig	4-werthig
	Mn = 55,1 / Fe = 56,0	Ni = 58,7	Co = 58,7
Differenz =	49,2 / 48,3	45,6	47,3
	Ru = 104,3	Rh = 104,3	Pd = 106,0
Differenz =	92,8 = 2·46,4	92,8 = 2·46,4	93,0 = 2·46,5
	Pt = 197,1	Ir = 197,1	Os = 199,0

	2-werthig	
	Zn = 65,0	Cu = 63,5
Differenz =	46,9	44,4
	Cd = 111,9	Ag = 107,94
Differenz =	88,3 = 2·44,2	88,8 = 2·44,4
	Hg = 200,2	Au = 196,7

Fig.III-12 (b).
(Lothar Meyer, 1864).

Entwurf eines Systems der Elemente von Lothar Meyer. 1868.

§ 91 Nicht gedruckt. Wiedergabe nach dem Manuscript.

1	2	3	4	5	6	7	8
		Al = 27,3 *)	Al = 27,3 *)				C = 12,00
		$\frac{28,7}{2}$ = 14,3					16,5
							Si = 28,5
							$\frac{89,1}{2}$ = 44,55
Cr = 52,6	Mn = 55,1	Fe = 56,0	Co = 58,7	Ni = 58,7	Cu = 63,5	Zn = 65,0	—
	49,2	48,3	47,3		44,4	46,9	$\frac{89,1}{2}$ = 44,55
	Ru = 104,3	Rh = 104,3	Pd = 106,0		Ag = 107,94	Cd = 111,9	Sn = 117,6
	92,8 = 2·46,4	92,8 = 2·46,4	93 = 2·46,5		88,8 = 2·44,4	88,3 = 2·44,15	89,4 = 2·44,7
	Pt = 197,1	Ir = 197,1	Os = 199,0		Au = 196,7	Hg = 200,2	Pb = 207,0

*) Im Original durchstrichen und durch daruntergesetzte Punkte wieder gültig gemacht. K. S.

9	10	11	12	13	14	15	16
			Li = 7,03	Be = 9,3			
			16,02	14,7			
N = 14,04	O = 16,00	Fl = 19,0	Na = 23,05	Mg = 24,0			
16,96	16,07	16,46	16,08	16,0			
P = 31,0	S = 32,07	Cl = 35,46	K = 39,13	Ca = 40,0	Ti = 48	Mo = 92	
44,0	46,7	44,51	46,3	47,6	42	45	
As = 75,0	Se = 78,8	Br = 79,97	Rb = 85,4	Sr = 87,6	Zr = 90	Vd = 137	
45,6	49,5	46,8	47,6	49,5	47,6	47	
Sb = 120,6	Te = 128,3	J = 126,8	Cs = 133,0	Ba = 137,1	Ta = 137,6	W = 184	
87,4 = 2·43,7			71 = 2·35,5				
Bi = 208,0			? Tl = 201?				

S. *L. Gmelin*, Hdb. 5. Aufl. I, 47 ff.; Münch. gel. Anz. 1850 Bd. 30, S. 261, 272, abgedr. Ann. Chem. Pharm. 1858. 105, 187; *J. Dumas*, C. r. 1857, t. 45, p. 709; auch Ann. Chem. Pharm. 105, S. 74 u. a.

Seite 7 hat man sich in der Weise seitlich an Seite 6 angereiht zu denken, dass N = 14,04 in Spalte 9 neben C = 12,00 in Spalte 8 zu stehen kommt, P neben Si, Sb neben Sn, Bi neben Pb. K. S.

Fig.III-13

(Lothar Meyer,1868:as published by Seubert,1895).

I	II	III	IV	V	VI	VII	VIII	IX
	B = 11,0	Al = 27,3		—		?In = 113,4		Tl = 202,7
				—			—	
	C = 11,97	Si = 28		—		Sn = 117,8		Pb = 206,4
			Ti = 48		Zr = 89,7		—	
	N = 14,01	P = 30,9		As = 74,9		Sb = 122,1		Bi = 207,5
			V = 51,2		Nb = 93,7		Ta = 182,2	
	O = 15,96	S = 31,98		Se = 78		Te = 128 ?		—
			Cr = 52,4		Mo = 95,6		W = 183,5	
—	F = 19,1	Cl = 35,38		Br = 79,75		J = 126,5		—
			Mn = 54,8		Ru = 103,5		Os = 198,6?	
			Fe = 55,9		Rh = 104,1		Ir = 196,7	
		Co =	Ni = 58,6		Pd = 106,2		Pt = 196,7	
Li = 7,01	Na = 22,99	K = 39,04		Rb = 85,2		Cs = 132,7		—
			Cu = 63,3		Ag = 107,66		Au = 196,2	
?Be = 9,3	Mg = 23,9	Ca = 39,9		Sr = 87,0		Ba = 136,8		—
			Zn = 64,9		Cd = 111,6		Hg = 199,8	

Differenz von I zu II und von II zu III ungefähr = 16.
Differenz von III zu V, IV zu VI, V zu VII schwankend um 46.
Differenz von VI zu VIII, von VII zu IX = 88 bis 92.

Fig. III-14 (Lothar Meyer, 1870).

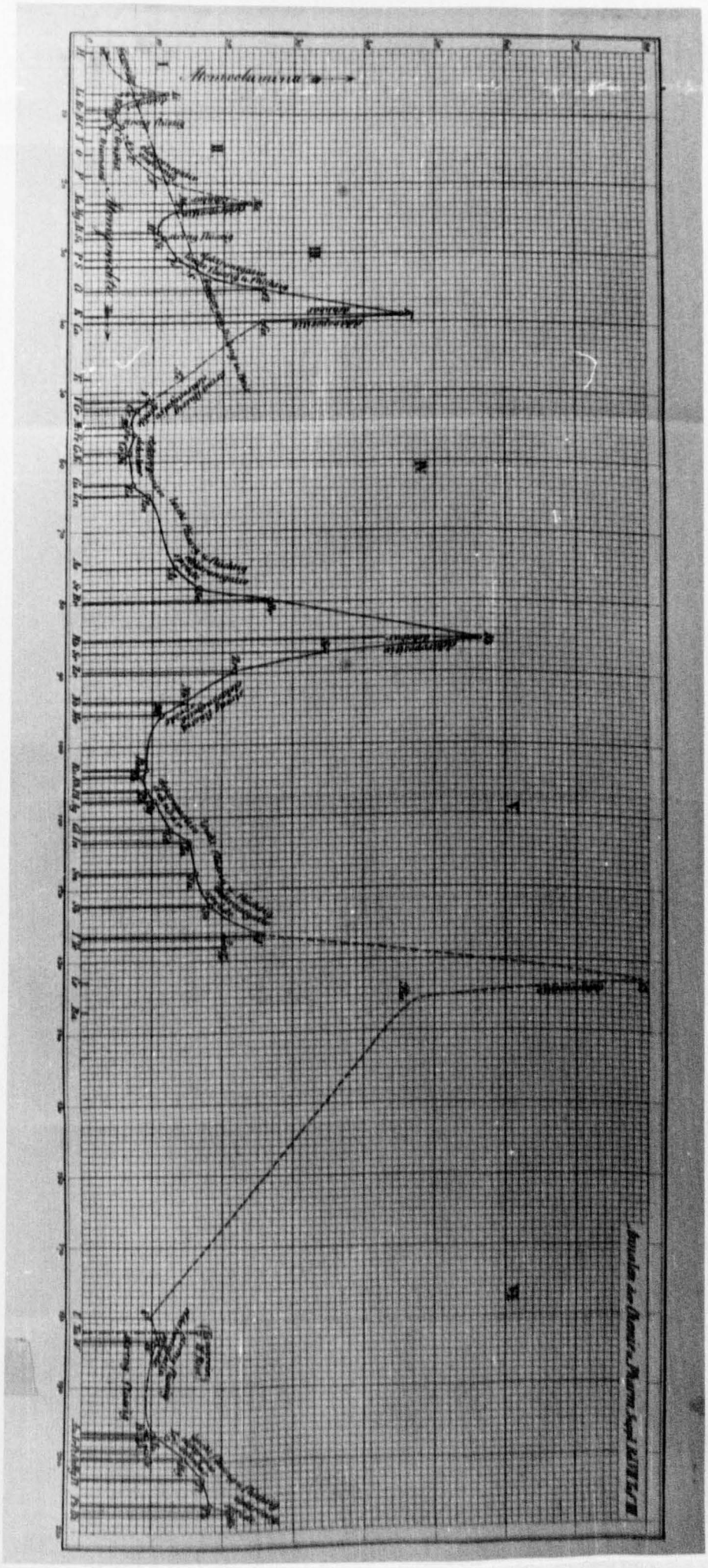

Fig.III-15.

(Lothar Meyer,1870:"atomic-volume" curve).

I								H 1	Li 7,01	Be 9,3
II	B 11,0	C 11,97	N 14,01	O 15,96	F 19				Na 22,99	Mg 23,94
III	Al 27,3	Si 28	P 30,96	S 31,98	Cl 35,37				K 39,04	Ca 39,90
IV	? 47?	Ti 48	V 51,2	Cr 52,4	Mn 54,8	Fe 55,9	Co 58,6	Ni 58,6	Cu 63,3	Zn 64,9
V	? 70?	? 72?	As 74,9	Se 78	Br 79,75				Rb 85,2	Sr 87,2
VI	? 88?	Zr 90	Nb 94	Mo 95,6	? 99?	Ru 103,5	Rh 104,1	Pd 106,2	Ag 107,66	Cd 111,6
VII	In 113,4	Sn 117,8	Sb 122	Te 128	J 126,53				Cs 132,7	Ba 136,8
VIII	? 173?	? 178?	Ta 182	W 184,0	? 186?	Os 198,6	Ir 196,7	Pt 196,7	Au 196,2	Hg 199,8
IX	Tl 202,7	Pb 206,4	Bi 207,5							

Spiral system of Meyer (1872).

Fig.III-16.

Meyer's "atomic-volume" curve (Fig.III-15), which graphically illustrates the periodic variation with increasing atomic weight of the "atomic volume" ($\frac{\text{atomic weight}}{\text{density of free element}}$) of the elements. In the course of constructing his "periodic" table of 1870 (Fig.III-14) Meyer had been led to alter the atomic weight of indium from its commonly-accepted value of ca. 75 (i.e. twice its equivalent) to the value 113.4(i.e. three times its equivalent), placing this element in the same row (family) of the table as B and Al. He suggested also that the atomic weight of uranium should perhaps be changed from 120 to 180, and proposed the need for a change in the accepted value for Ce[163]; neither U nor Ce is included in his table, but U (180) is included in the atomic-volume curve. Having made such suggestions, however, Meyer concluded his paper of 1870 with a note of caution: "It would be rash to change the accepted atomic weights on the basis of so uncertain a starting-point [sc. as the periodic system]".[164] Although Meyer had marked a number of empty spaces in his table of 1870, he did not discuss the significance of such gaps.

The periodic system of the elements provided the classificatory basis for the 2nd (1872) and subsequent editions of Meyer's Die modernen Theorien. It was not until after 1880, following a priority dispute with Mendeleev, that Meyer's contribution to the emergence of the periodic system came to be widely recognised.

6. D.I. Mendeleev: 1868-1871

During the period 1868-71 Mendeleev, by that time a professor of chemistry at St. Petersburg University, wrote the first edition of his textbook on general chemistry, Osnovy Khimii (Principles of Chemistry). While working on this book Mendeleev came to seek some strict scientific basis upon which he could organise the presentation of his treatment of the chemical elements. His reflections on this problem led him, in early 1869, first to jot down rough outlines of comparisons among the elements and among groups of elements, and then to attempt construction of a single classificatory system which included all of the elements. By 17th February (O.S.; 1st March, N.S.) he had drawn up a fair-copy manuscript table of the elements which he entitled Opyt sistemy elementov, osnovannoi na ikh atomnom vese i khimicheskom skhodstve (Attempt at a system of the

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[163] Ibid., p.17.

[164] Ibid.

elements, based upon atomic weight and chemical resemblance).[165] On 1st March (O.S.; 13th March, N.S.) printed versions of this table[166] (some in Russian, some in French) were sent by Mendeleev to various Russian and foreign chemists;[167] and later in the same month a German version of the table was published in the Journal für praktische Chemie.[168]

While clearly defective in certain respects as a solution to the problem of classifying all of the elements into a single "natural" system,[169] Mendeleev's Attempt at a system would seem to come close enough to being an all-embracing system of elements in which is shown a fairly regular recurrence ("periodicity") of similar properties with increasing atomic weight, to justify its later recognition as being an early form of periodic table (viz. the first type of periodic table to be published by Mendeleev).[170]

In March 1869 Mendeleev wrote an article entitled Sootnoshenie svoistv s atomnym vesom elementov (Correlation of the properties of the elements with their atomic weights),[171] in which he presented his discovery of the periodicity of properties of the elements, and discussed his Attempt at a system. This was read as a paper to a meeting of the Russian Chemical Society

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[165] Table 3(M3), Ch.IV. The particular arrangement of elements given in this table - and in the corresponding published tables, table 8 (P1) and table 9 (P2) in Ch.IV - will in future discussions be referred to as Mendeleev's Attempt at a system.

A detailed account of the path by which Mendeleev discovered the periodic law (including an attempt at a psychological analysis), interpreted in terms of Marxian-Engelian-Leninist dialectics ("logic"), has been given by Kedrov, e.g. in Bibl.44. Kedrov sees Feb. 17th (O.S.) 1869 as "the day of the discovery of the periodic law".

[166] Table 8(P1) in Ch.IV.

[167] The Russian version of this table was included in the second instalment (vypusk) of Pr.Ch., R-1, part I, published in March (O.S.) 1869.

[168] J. für prakt. Chem. [1], 106 (1869) 251.

[169] Mendeleev himself (see later) acknowledged his Attempt at a system as being defective in two main respects: the halogens and the alkali metals, two families of sharply distinct properties, are juxtaposed in the table; and indium, thorium and the rare-earth elements are placed unsatisfactorily, in two tails of the table which break the atomic-weight sequence.

[170] For a consideration of the problem of judging whether or not a particular classificatory system can be acknowledged as being a "periodic system", see Ch.VIII.

[171] Henceforth in this thesis referred to as Correlation of properties.

on 6th March (O.S.; 18th March, N.S.),[172] and published in the Journal of the Society in May.[173]

Mendeleev began this article by critically assessing various earlier attempts at classifying the chemical elements. He criticised division of the elements into metals and non-metals as being not rigidly applicable, and as being in certain respects chemically unnatural. Classificatory systems based upon "the relationship of the elements to hydrogen and oxygen"- by which expression Mendeleev seems to have meant both ability to combine with hydrogen or oxygen, and also stability of any resulting compounds - he rejected on the grounds that they "force us to keep apart members which undoubtedly show great resemblance", e.g. fluorine and iodine.[174] On the question of arranging the elements into an electrochemical series, or some other such series of "relative affinity", Mendeleev remarked, "With such diverse relationships as exist among the simple bodies, it is impossible to think of presenting their system in the form of a single continuous (nepreryvnogo) series."[175] Classification of the elements on the basis of valency ("atomicity") was rejected as being artificial in those cases which recognised a fixed (single-valued) valency for each element, and as involving too much uncertainty in the case of any attempt which recognised variable (many-valued) valency. It is interesting that Mendeleev here explicitly rejected the idea of a system based upon maximum valency (citing the case of hydrogen peroxide as a particular difficulty when considering the valency of hydrogen),[176] when only six months later he had come to consider maximum valency in "saline", or "non-peroxide", oxides to provide one of the main chemical foundations of his periodic system (see later). In concluding his assessment of earlier attempts at classification of the elements Mendeleev referred to the various attempts which had been made to discover lawfulness in the relationships within natural family groups of elements (such as the

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[172] The paper was read by N.A. Menshutkin (see p.17).

[173] J.Russ.Chem.Soc., 1 (1869) nos. 1 and 2, pp.60-77. Reprinted in PLBA, 10-31.

[174] J.Russ.Chem.Soc., 1869, pp.60-1.

[175] Ibid., p.61. By "a single continuous series" Mendeleev is here referring to a one-dimensional system, such as the electrochemical series. His own periodic system, although based upon an ordering of the elements into a single series according to increasing atomic weight, incorporates also a second dimension, viz. that of chemical analogy.

[176] Ibid., p.62.

halogens, alkali metals, etc.). Mentioning by name in this connection Kremers, Lenssen, Dumas, Pettenkofer and Sokolov, and acknowledging that others had also contributed in this field, Mendeleev expressed the view that apart from Lenssen none of these earlier workers had satisfied the "natural demand" for a single classificatory system for all elements.[177] On the other hand, Mendeleev felt that Lenssen's attempt was defective on the grounds both of unnatural grouping, and of lack of provision for possible new elements. Mendeleev singled out Kremers as having discovered certain relationships not only within families of elements, but also between some of these family groups.

By the time his article Correlation of properties was published Mendeleev had appended to it a footnote, dated 5th April (O.S.) 1869, in which he refers to Odling's system of 1865 given in the latter's A course of Practical Chemistry arranged for the use of medical students:[178]

> ... in the April meeting [sc. of the Russian Chemical Society][179] F.N. Savchenkov told me that Odling had included a table like mine on p.224 of his "Course of Practical Chemistry" (translated by Savchenkov, 1867).[180] However, Odling said nothing about the significance of his table and, as far as I know, has nowhere recalled it.[181] Until now it was completely unknown to me, as, probably, also to the majority of scientists. If Odling had attached any theoretical significance to his table he probably would have written on this subject, one which in my opinion touches upon the fundamental questions of chemistry. In his book this table is headed simply: "Atomic Weights and Symbols of the Elements".[182]

No reference was made by Mendeleev in his Correlation of properties to the earlier classificatory work of de Chancourtois, Newlands and

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[177] Ibid., p.65.

[178] This is the system presented in Fig.III-8, earlier in this chapter.

[179] Mendeleev is here referring to his Attempt at a system - see tables 8(P1) and 9 (P2), Ch.IV.

[180] Savchenkov's translation into Russian of Odling's book was published as Kurs prakticheskoi khimii, St. Petersburg.

[181] Mendeleev here appears to have been unaware of Odling's paper of October 1864 and his contribution to Watts' Dictionary in 1865, in both of which Odling had given a table very like that in his A course of Practical Chemistry (1865) and had concluded that the arithmetic weight-relationships shown in the table "are too numerous and decided not to depend upon some hitherto unrecognised general law" (Odling, Bibl. 85, 1865, p.648; Bibl.129, vol. III, 1865, p.976).

[182] J.Russ.Chem.Soc., 1869, p.76, footnote.

Lothar Meyer. He seems to have not yet known of de Chancourtois' and Newlands' contributions[183] (twenty years later he was to recognise in their work of the 1860's "an approach to the periodic law, and even its germ"[184]). Whether Mendeleev already knew of Lothar Meyer's classification of 1864 is not clear, but in any case he later claimed that this classification was no more than "a simple collocation of groups of analogous elements".[185]

Mendeleev's account in Correlation of properties of his own attempts to classify the chemical elements into a single system was introduced with a passage in which he indicates the nature of his motivation in this direction, and the reason for his using atomic weight as a basis for classification:

> While compiling a chemical manual entitled "Principles of Chemistry" I felt obliged to dwell upon the question of a system for the simple bodies, so as to be guided in my arrangement of them not by accident or instinct, but by some precise and definite principle ... Any system based upon precisely observed numbers is of course already preferable to systems which have no numerical basis, since the scope for arbitrariness in a numerically-based system is small ... No matter how the properties of a simple body may change in the free state, something remains constant, and when the elements form compounds this something ... establishes the characteristics of the compounds which include the given element.[186] In this respect we know at present only one numerical property peculiar to the element, namely the atomic weight. The magnitude of the atomic weight ... is a number which relates to ... that material part which is common to the simple body and all its compounds ... The way in which Gerhardt and Cannizzaro determined the atomic weights of the elements is based upon such unshakeable and indubitable methods that for the majority of bodies, in particular for those simple bodies whose specific heats in the free state have already been determined, there will arise no doubts about the atomic weights of the element - unlike the situation of a few years ago when atomic weights were so frequently confused with equivalents, and determined on the basis of various, often conflicting, principles.
>
> This therefore is the reason for my attempting to base a system upon atomic weight.[187]

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[183] Mendeleev himself later claimed not to have known of the work of de Chancourtois and Newlands at the time of his discovery of the periodic law, e.g. see Pr.Ch., R-8 (1906) n.405. Although such autobiographical remarks are not always reliable, there is no evidence to suggest that this claim by Mendeleev is not true; in fact the poor response to the contributions of de Chancourtois and Newlands at the time of their presentation makes it rather unlikely that Mendeleev should have heard of this work by 1869.

[184] Faraday Lecture, 1889: PLBA, 213. See also Pr.Ch., R-8 (1906) n.405.

[185] 1871: PLBA, 390. (See Ch.VIII for detailed reference, and for an assessment of the justification of this claim).

[186] See pp.30ff (Ch.I - on Mendeleev's doctrine of the chemical elements).

[187] J.Russ.Chem.Soc., 1869, pp.65-7.

Mendeleev then goes on to discuss the results of his attempts to classify the elements according to atomic weight. "All collations made by me in this direction", he says, "lead me to the conclusion that the magnitude of the atomic weight determines the nature of an element, just as the weight of the molecule determines the properties and many of the reactions of compound bodies".[188] This rather weak statement of the existence merely of an unspecified lawlike correlation between atomic weight and chemical properties is made more specific by Mendeleev later in the same article: "The elements, arranged according to the magnitude of their atomic weights, present a clear periodicity (periodichnost') of properties".[189] In a manuscript draft of this conclusion Mendeleev had expressed himself even more fully:

> The elements, arranged according to the magnitude of their atomic weights, present a periodic function, so that if we should manage to express the chemical properties of each element by a number, and if we take axes and place the atomic weights along the abscissa and the properties along the ordinate, then we should obtain a wave-like (volnoobraznaia) curve, the bends in which show a similarity of outline in the different parts of the curve (izgiby kotoroi predstavliaiut skhodstvo ochertanii v raznykh chastiakh krivoi).[190]

Two features of the dependence of the properties of the elements upon atomic weight are indicated in these remarks by Mendeleev: a common pattern of dependence for different properties; and the fact that this common pattern of dependence is "periodic". The existence of a common pattern of variation with atomic weight (or, at least, of close parallels in the pattern of variation) for different properties is reflected in the very existence of chemical families of analogous elements, and is therefore assumed (albeit usually tacitly) in any recognition of families of analogous elements: the existence of a family of analogous elements reflects the concurrence in various elements (or, at various atomic-weight values) of a certain characteristic set of values or qualities for a corresponding set of different properties - in the case of the alkali metals, for example, the concurrence of the properties of monovalence, strong basicity, and in the free state metallic character, low melting-point, softness, etc. The recognition of such chemical families was fundamental to Mendeleev's classification of the elements; it is clearly implicit in his above-quoted

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[188] Ibid., p.69. (See n.101, below).

[189] Ibid., p.76.

[190] Sc.Ar., 28.

references to "a clear periodicity of properties" and "a periodic function" (in the singular rather than the plural). From the last of the above-quoted passages (i.e. the manuscript draft) we see that Mendeleev characterises the "periodicity" of the common variation of different properties of the elements with increasing atomic weight as a "wave-like" variation, "the bends in which show a similarity of outline in the different parts of the curve". The term "wave-like" indicates not only regular recurrence after certain intervals, but also regular and gradual change within the periods, which is indeed the nature of the "periodicity" of the elements as illustrated in the periodic system. Later, in the 3rd (1877) and subsequent editions of his Principles of Chemistry, Mendeleev was to describe this particular nature of the "periodicity" of the elements more clearly: "With increase of mass [sc. of atomic weight] the properties at first change gradually and regularly, and then return to the original, and again a new period of change of properties begins, like the previous one".[191]

Having expressed what he refers to as the "law" (zakon) or "principle" (nachalo) that "the magnitude of the atomic weight determines the nature of an element", Mendeleev in his article Correlation of properties turned to the problem of constructing classificatory systems on the basis of this "principle",[192, 193] presenting a version of his Attempt at a system[194] with the following remarks:

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[191] Pr.Ch., R-3 (1877) 882 (PLSM,354); R-8 (1906) 258 (PLBA, 297).

[192] Although in his Correlation of properties Mendeleev already talks of the "periodicity" of properties of the elements, his first published use of such terms as "periodic lawfulness", "periodic law", "law of periodicity", "principle of periodicity", and "periodic system", "periodic table", did not appear until 1871 (see later). He does, however, refer to the "law of periodicity" in a manuscript draft of the conclusions of his Correlation of properties (see Sc.Ar., 29).

[193] That a distinction may be drawn between the periodic law and the periodic system has been pointed out by D.N. Trifonov in the following passage:

"Mendeleev's doctrine of periodicity includes two basic conceptions: 1) that of the law of periodicity and 2) that of the periodic system. The law is the reflection of the fundamental fact of the periodic change of the properties of the elements when the latter are arranged in a natural series in accordance with the magnitude of the numerical value of a certain parameter (atomic weight or nuclear charge) ... The conception of the 'periodic system' does not have such a clear definition. The system may be characterised as a natural classification of the chemical elements, based upon the law, and appearing as a concretised reflection of the latter". (Avtoreferat of Bibl. 121, p.3).

[194] Table 9(P2), Ch.IV; this differs from table 8(P1) only in having the entry Bi = 210 instead of Bi = 210?.

From now on in this thesis references to Mendeleev's periodic tables will give the appropriate table-numbers as presented in Ch.IV without appending the chapter-reference "Ch.IV".

I now present one of the many systems of the elements which are based upon atomic weight. It serves only as a trial, an attempt at an expression of the sort of result which may be achieved in this connection. I myself see that this attempt is not final (*), but it seems to me that it already expresses the applicability of my proposed principle to the totality of elements whose atomic weights are known with certainty. And on this occasion my main desire has been to find a general system of the elements. Here is this attempt:

[Table 9 (P2)]

(*)Perhaps it would be more rational to arrange the accompanying table as:[195]

above	Li	Na	K	Rb	Cs	Tl
	-	-		Ba	Sr	Pb
then	-	-	Cr	Mo	-	-
	-	-	V	Nb	Ta	etc.
below	O	S	Se	Te	-	-
	F	Cl	Br	J	-	-

We should then have the advantage that such sharply distinct elements as Cl and Na would constitute the extreme rows, between which would be arranged the elements of milder chemical character. But in this case the middle of the table would be almost empty, and extremely doubtful, whereas at present [sc. in table 9(P2)] the distribution in the middle is without doubt and includes many members, all the lesser-known elements (corps à serier) standing at the edges, above and below. Further, between the extreme rows

Li	Na	K	Rb	Cs
F	Cl	Br	J	

there is no proper correspondence of differences:

$$\left.\begin{matrix}\text{Li} = 7\\ \text{F} = 19\end{matrix}\right\}12 \qquad \left.\begin{matrix}\text{Na} = 23\\ \text{Cl} = 35.5\end{matrix}\right\}12.5 \qquad \left.\begin{matrix}\text{K} = 39\\ \text{Br} = 80\end{matrix}\right\}41 \qquad \left.\begin{matrix}\text{Rb} = 85\\ \text{J} = 127\end{matrix}\right\}42,$$

and therefore we would have a distinct variation of differences between the various rows, which is not found for the main members of the proposed table [sc. for the central region of table 9(P2)]. Or else we are obliged to assume very many missing members in drawing up the system. Neither is of much use. Besides, it seems to me the most natural to construct a cubic system[196] (the proposed system is a planar one), but the attempts at its construction also have not led to a suitable result. The following two attempts show what diversity of collocation is possible with the assumption of the basic principle expressed in this

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[195] There are three apparently unintentional errors in this "more rational" table: i) Ca is omitted from the second row; ii) Ba and Sr are the wrong way around; and iii) the 3rd and 4th rows are the wrong way around. In the reprint of Correlation of properties given in PLBA Kedrov has "corrected" errors i) and iii) (see PLBA, 22 and 688).

[196] An account of Mendeleev's consideration of various types of periodic system is given in Ch.V.

article [sc. assuming the periodicity of properties of the elements with increasing atomic weight].

[Table 10 (P3)][197]

In addition to this, the series Cr, Mn, Fe, Ni, Co should provide a transition (atomic weights 52 to 59) from the lower part of the 3rd column (which contains K, Ca, V) to the upper part of the 4th column (i.e. to Cu), as also Mo, Rh, Ru, Pl provide a transition from the 5th column to the 6th (to Ag), and Au, Pt, Os, Ir, Hg? from the 8th to the 9th.[198] A spiral [sc. 3-dimensional spiral] system is obtained. In this system resemblance is observed primarily in the alternate members of the rows, e.g. in the 2nd row Be, Ca, Sr, Ba, Pb, and similarly Mg, Zn, Cd.[199] The atomic-weight differences here are almost the same for each vertical and horizontal row. If we separate out from this system the most similar members, we obtain a system of the following kind:

Above will be:

Li	K	Rb	Cs
Be	Ca	Sr	Ba

In the middle will be:

O	-	-	-
F	-	-	-
Na	Cu	Ag	-
Mg	Zn	Cd	-

And below will be:[200]

S	Se	Te	
Cl	Br	J	-

A large number of such distributions is possible. They do not alter the essence of the system. Everything that is expressed in these systems appears also in that which I propose as an attempt at such a system [sc. table 9 (P2)]. [Op.cit., pp. 69-71]

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[197] Spronsen (Bibl.110, pp. 135, 220) refers to this table as Mendeleev's "spiral" or "screw-shaped" system (see Ch.V).

[198] Thus, in his very first article on the periodic law Mendeleev recognised the iron, palladium and platinum groups as "transition" groups (see also later in the same article - op.cit., p.73). He referred to the "transitional" character of these elements also in his second and third articles on the periodic law (see PLBA, 34; 53, 57). On the question of Mendeleev's placing of Cr, Mn and Mo in the periodic system see later in the present chapter, and section C of Ch. VI.

[199] We see here a recognition by Mendeleev of sub-groups of elements.

[200] Tungsten, W, seems to have been unintentionally omitted from the space following Te in this table (Kedrov, PLBA, 689, has made the same observation; and in the reprint of Correlation of properties in PLBA has included W in this space).

Mendeleev's appreciation even at this time of various inadequacies of his Attempt at a system was expressed again later in the same article: "There arises a complete doubt regarding the positions of certain elements. This concerns those elements which have been studied little, and whose atomic weights have hardly been established with certainty, e.g. yttrium, thorium and indium ... The proposed system of the elements certainly cannot be considered as final ...".[201]

In concluding his Correlation of properties Mendeleev presented the following summary of results:

1. The elements, arranged according to the magnitude of their atomic weights, present a clear periodicity of properties.[202]

2. Chemically similar elements have atomic weights whose values are either close (such as Pt, Ir, Os) or else successively and uniformly increasing (such as K, Rb, Cs). The uniformity of the increase for different groups was concealed from previous observers[203] because in their collations they did not make use of the deductions of Gerhardt, Regnault, Cannizzaro and others who have established the true (istinnuiu) values of the atomic weights of the elements.

3. The arrangement of the elements or their groups according to atomic weight corresponds to their so-called atomicity [sc. valency][204], and to some extent to difference of chemical character - as is clearly evident in the series,

Li, Be, B, C, N, O, F,

and is repeated in the other series.

4. The simple bodies which are most widely distributed in nature have small atomic weights, and all elements with small atomic weights are characterised by a distinctiveness (rezkost'iu) of properties. They are therefore the typical (tipicheskie) elements. Hydrogen, as the lightest element, can justifiably be considered the most typical.[205]

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[201] Op.cit., p.73.

[202] It should perhaps be pointed out that Mendeleev was fully aware of the notable exception to this generalisation which is provided by the property of the specific heat of the simple substances: according to the law of Dulong and Petit, sp.ht. of solid simple substance x atomic weight of the element (the "atomic heat") = a constant.

[203] Mendeleev's footnote of 5th April (O.S.) 1869 on Odling's work, quoted above, was appended here.

[204] Mendeleev is here referring to the "usual" valency of the elements, e.g. monovalence for the halogen elements (see later in the present chapter).

[205] This conclusion summarises a discussion presented by Mendeleev on pp.74-5 of Correlation of properties, where he draws an analogy between the fact that "in the lowest members of the rows [sc. of his Attempt at a system], compared with the higher members, a greater distinctiveness and clarity of properties and reactions is noticeable", and the fact that "in the higher members of homologous series there is a smoothing-out of certain peculiar features of the series". The term "typical" to designate the lightest elements clearly incorporates for Mendeleev the sense of "showing the most

5. The magnitude of the atomic weight determines the character of an element, just as the magnitude of the molecule determines the properties of a compound body.[206] In studying compounds we should therefore pay heed not only to the properties and quantities of the elements, not only to their interactions, but also to the weights of their atoms.[207] Thus, for example, the compounds of S and Te, and of Cl and I, etc., although similar show also extremely clear differences.

6. We must expect the discovery of many yet unknown elements, e.g. elements analogous to Al and Si, with atomic weights 65-75.[208]

7. The value of the atomic weight of an element may sometimes be corrected in the light of our knowledge of its analogies. Thus, must not the atomic weight of Te be 123-126, and not 128?[209]

8. Certain analogies of the elements come to light through the magnitude of their atomic weights. Thus, uranium is shown to be an analogue of boron and aluminium, as is justified by a comparison of their compounds.[210]

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distinctive properties": the "typical" elements represent a "type" or "pattern" which is mirrored in the heavier elements with a certain loss of distinctiveness, this smoothing-out of distinctive properties increasing with increasing atomic weight. What Mendeleev means by the statement that hydrogen is the "most typical" element is not really clear, although he presumably means that the essential quality of "elementness" (whatever that may be) is shown more distinctly in hydrogen than in any other element.

[206] In a manuscript draft of this conclusion Mendeleev is more explicit: "... just as the magnitude of the molecular weight determines the physical properties of the bodies, and their quantitative ratios in chemical reactions" (Sc.Ar., 28-9). In the 3rd (1877) and subsequent editions of Pr.Ch. Mendeleev wrote: "The weight or mass of molecules ... determines many properties of the molecules independently of their composition. Thus, CO and N_2 are two gases of the same molecular weight, and many of their properties (density, condensation-point, specific heat, etc.) are identical or nearly so. The differences depending on the nature of the substance play another role, giving rise to magnitudes of another order. The properties of the atoms are primarily determined also by their mass or weight, standing in periodic dependence upon it" (Pr.Ch., R-8, 1906, 258; PLBA, 296).

[207] Mendeleev here appears to be pointing to the need to recognise not only the general family characteristics of an element but also its individual characteristics, the latter depending upon the particular atomic-weight value of the element.

[208] Such expectations arose for Mendeleev from the presence of gaps in the periodic system (see Ch.VI).

[209] See Ch.VI.

[210] Op.cit., pp.76-7.

Mendeleev's last words in this article, following immediately after conclusion 8 of the above-quoted summary of results, were:

> The aim of my article will have been completely achieved if I succeed in turning the attention of investigators to the relationships between the atomic weights of dissimilar elements - a subject which as far as I know has so far received almost no attention. Believing that in problems of this sort lies the solution of some of the most important questions of our science, I myself intend, as far as time allows, to turn to a comparative study of lithium, beryllium and boron.[211]

Mendeleev's Attempt at a system and his article Correlation of properties did not attract much attention in the scientific community of the time, either in Russia or elsewhere. The majority of Russian chemists were working in the field of organic chemistry, and to them Mendeleev's first contribution on the subject of the periodicity of the elements would have seemed a theoretical speculation of no more than minimal and passing interest, far removed from the world of chemistry as they knew it. Outside Russia, acquaintance with Mendeleev's Russian-language work would have been negligible, the initial knowledge of his first work on periodicity being obtained from those printed copies of Attempt at a system which Mendeleev himself had sent to various chemists abroad (March 1869), from the version of this table published in the Journal für praktische Chemie (March 1869), and (probably mainly) from an abstract of Correlation of properties published in German in Zeitschrift für Chemie (June or July 1869).[212] This German abstract began with the sentence, "If we arrange the elements in vertical rows in order of increasing atomic weight so that the horizontal rows contain analogous elements, also arranged according to increasing atomic weight, then the following result is obtained". Mendeleev's Attempt at a system was then presented,[213] followed by the 8 conclusions outlined by Mendeleev at the end of his Correlation of properties. However, in the German abstract these conclusions suffer from such mistranslation, omission and crude error that much of their significance as presented in the Russian original has been lost. For example, in conclusion 1 of the German abstract Mendeleev's original "The elements ... present a clear periodicity (periodichnost') of properties"

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[211] Ibid., p.77. For a brief manuscript relating to the comparative study of Li and Be by Mendeleev, apparently dating from March or April 1869, see Sc.Ar., 18.

[212] Ueber die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente, Zeitschrift fur Chemie, 12 (1869) 405-6.

[213] Table 8 (P1) is given in this abstract, even though it was actually table 9 (P2) which appeared in Mendeleev's Correlation of properties. The difference between the tables is, however, negligible (see above, n.185).

is translated as "The elements ... show a stepwise (stufenweise)change in properties". Also, the statement of periodicity at the end of the original conclusion 3 - "and is repeated in the other series" - has been completely omitted from the German version. And in conclusion 8 of the German abstract we find the strange comment, "Thus Bo (?) is shown to be an analogue of Bo and Al", rather than Mendeleev's original, "Thus uranium is shown to be an analogue of boron and aluminium". In view of this misrepresentation of Mendeleev's results, coupled with the obvious defects of his Attempt at a system, it is hardly surprising that Mendeleev's first contribution on the subject of the periodicity of the elements should have aroused little initial reaction abroad.[214]

After preparing the article Correlation of properties Mendeleev began (probably in May 1869) to study the dependence upon atomic weight of the atomic volumes of the elements (both as free elements, and also in combination in certain types of compound). He organised his results into a paper entitled Ob atomnom ob"eme prostykh tel (On the atomic volumes of the simple bodies),[215] which he read to a meeting of the Chemical Section of the 2nd Congress of Russian Scientists and Physicians in Moscow, 23rd August (O.S.; 4th Sept., N.S.) 1869. In this paper Mendeleev concluded that atomic volume shows a periodic dependence upon atomic weight, in accordance with the periodicity expressed in his classificatory system of the elements. A short abstract was published at the time of the Congress;[216] but the full paper, containing tables 14 (P5) and 15 (P6), was not published until the spring of 1870,[217] by which time Lothar Meyer's article Die Natur der chemischen Elemente als Function ihrer Atomgewichte - which also included a

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[214] Kedrov (Sc.Ar., 68) has said of the misrepresentation of Mendeleev's results in the Zeitschrift abstract: "These distortions could not have been accidental; they testify to a clear ill-intention on the part of the author of the abstract, who distorted the fundamental content of the great discovery made by a Russian scientist, and attempted to present this discovery in the form of a simple reduction of the elements into a table. As a result of this, beginning from the middle of 1869 foreign scientists were incorrectly informed about the very essence of the great discovery made by Mendeleev".

[215] Henceforth in this thesis referred to as Atomic volumes.

[216] See PLBA, 605-6; or Sc.Ar., 75.

[217] Trudy 2-go s"ezda russkikh estestvoispytatelei i vrachei v Moskve, 1870, ch. 1, otd. 2, str.62-71. Reprinted in PLBA, 32-49. This "full" version of the paper omitted the reference to "Prout's hypothesis" which had been included in the abstract published earlier (see Ch.II, p.89).

consideration of the periodicity of atomic volume - had already been published (in March 1870). The following note on Meyer's paper was appended by Mendeleev to the proof-copy of his own article on Atomic volumes:

> That which has been presented here was communicated by me to a congress in August 1869. In Liebig's Annalen for 1870 there has appeared (after I had sent my own article for printing) an article by Lothar Meyer on the same subject. Meyer's conclusions are based upon an assumption of that system of elements which was proposed by me, and are in agreement with my own conclusions in connection with atomic volumes. He, too, pays particular attention to the descending and ascending series of elements, and to the successiveness of the change in volumes. But the deductions have gained in clarity from the graphical presentation included with his article [sc. Meyer's atomic-volume curve]. In making this note I have no desire to raise the question of scientific priority (in my opinion these questions have no scientific interest), but wish only to point to the table appended to Meyer's article as being an eye-catching means of expressing those complex relationships which I have pointed to in the foregoing lines.[218]

After the Moscow Congress of August (O.S.) 1869 Mendeleev turned his attention from the study of "physical" functions of atomic weight (viz. the dependence of atomic volume upon atomic weight) to that of "chemical" functions - specifically, to the study of the dependence upon atomic weight of the composition of the highest salt-forming, or "saline", oxides of the elements.[219] On 2nd October (O.S.; 14th Oct., N.S.) 1869 the results of his investigations in this direction were communicated by Mendeleev to a meeting of the Russian Chemical Society in a paper entitled O kolichestve kisloroda v solianykh okislakh i ob atomnosti elementov (On the quantity of oxygen in saline oxides and on the atomicity of the elements).[220] In this paper Mendeleev concluded: "The natural distribution of elements by groups on the basis of atomic-weight value corresponds to that quantity of oxygen which these elements can hold in their highest saline oxides ... The chemical properties of the elements are a periodic function of atomic weight".[221] The paper itself, containing the table 13 (P4), was not published until January 1870,[222] but a report of it by V. von Richter appeared (in German) in Berichte

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[218] Ibid. (Trudy, 1870), p.71.

[219] Mendeleev's classification of oxides into "saline" oxides and "peroxides" is discussed in Ch.V.

[220] Henceforth in this thesis referred to as On the quantity of oxygen.

[221] PLBA, 57, 58.

[222] J.Russ.Chem.Soc., 2 (1870) 14-21. Reprinted in PLBA, 50-8.

in late October 1869.[223] Richter began his report by recalling the abstract of Mendeleev's Correlation of properties which had been given in Zeitschrift für Chemie, and then continued -

> Starting from the view that atomic weight truly constitutes an essential constant for the elements, Mr. Mendeleev considers that atomic-weight value gives a true basis for the classification of the elements. The incompleteness of our knowledge of the known elements forces us to consider as only provisional the many various groupings which have so far been assumed [sc. by Mendeleev],[224] but Mr. Mendeleev is sure that the principle rests on a real basis.

Richter then presented a partial version of table 13 (P4), followed by a brief summary of the results arrived at in On the quantity of oxygen. His final comment was, "I think that this interesting formulation (Formulierungen) will not be slow in arousing your attention".[225]

With this report by Richter there were now three instances of publication in German journals of Mendeleev's results on the subject of the periodicity of properties of the chemical elements (the other two being the version of Attempt at a system given in the Journal für praktische Chemie, and the abstract of Correlation of properties in Zeitschrift für Chemie). Such was the state of the German literature when Lothar Meyer wrote his first paper on periodicity, in December 1869.

In the autumn of 1870 Mendeleev began to prepare an article with the title of K sisteme elementov (Towards a system of the elements). In early November, having already drafted at least 3 manuscript variants of this proposed article,[226] Mendeleev decided to divide it into two separate parts for publication: one part to deal in some detail with the question of changing the accepted atomic-weight values of certain elements, and the other to deal with the prediction of new elements and their properties on the basis of the periodic system. The first part was completed on 17th November (O.S.; 29th Nov., N.S.), and read by Mendeleev to a meeting of the St. Petersburg Academy of Sciences on 24th November (O.S.; 6th Dec., N.S.). It was published, in German translation, in the Bulletin of the Academy in March 1871, as Über die Stellung des Ceriums im System der Elemente (On the place of cerium in the system of the elements).[227] The second part was

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[223] Berichte, 1869, B.II, S.553. Reprinted in Sc.Ar., 88-9.

[224] Ibid.

[225] Ibid.

[226] See Sc.Ar., 121-37.

[227] Bull.de l'Acad. des Sc., St.Pet., 16 (1871) 45-51. A Russian version is given in PLBA, 59-67. This paper will be referred to henceforth in this thesis as On the place of cerium. Its contents will be discussed mainly in Chs. VI and VII.

completed by Mendeleev on 29th November (O.S.; 11th Dec., N.S.), and published, in Russian, in February 1871 in the Journal of the Russian Chemical Society, as Estestvennaia sistema elementov i primenenie ee k ukazaniiu svoistv neotkrytykh elementov (A natural system of the elements and its use for indicating the properties of undiscovered elements).[228]

With On the place of cerium was published table 33 (P10);[229] with A natural system of the elements, table 30(P7). In these (very similar) tables the major defects of Mendeleev's Attempt at a system had been remedied to the extent that Mendeleev felt justified in calling his new arrangement a "natural system" of the elements. In his article A natural system of the elements he had the following to say on this matter:

> The distribution of the elements according to the magnitude of their atomic weights in that form which was suggested by me last year [sc. in Attempt at a system] ... had two important defects: first, the fact that some of the elements - viz. uranium, indium, and the cerite elements [sc. cerium and its analogues] - did not find their proper place in this system, and it may therefore have been thought that the principle of the periodic dependence of properties upon the magnitude of the atomic weight - which lies at the base of my suggested system - does not possess that degree of generality which should be possessed by the principles of a natural system; and secondly, in that form of arrangement of the elements which was proposed by me, and which seemed to me then to be the most convenient for the expression of all of the relationships, the chemically most distinct groups of elements - the alkali metals and the halogens - were juxtaposed ... These two defects of that system of the elements which was originally proposed by me may already at the present time be eliminated much more completely than has previously been possible; and as a result we are now able ... to lay down the basis for a completely natural system of the elements ...
>
> When ... the most important obstacle to the application of the principle of periodicity (nachala periodichnosti)[230] to the totality of the elements had been eliminated (by the determination of the places of Ur, Th, Ce, In), I considered it profitable to attempt anew to refine the system of elements which had been proposed by me, and the accompanying table [sc. table 30 (P7)] expresses the results of this

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[228] J.Russ.Chem.Soc., 3 (1871) 25-56. Reprinted in PLBA, 69-101. This paper will be referred to henceforth in this thesis as A natural system of the elements. Its contents are considered primarily in Ch. VI.

[229] Table 33 (P10) as given in Ch.IV is a Russian version of the table which was originally published in German.

[230] This appears to have been the first published use by Mendeleev of the term "principle of periodicity" or any similar term (such as "law of periodicity", "periodic law", "periodic lawfulness") (see n.183, above). The term "periodic lawfulness" (periodische Gesetzmässigkeit) appeared in his On the place of cerium which although written earlier was published later. In the 2nd part of Pr.Ch., R-1, published in March 1871, Mendeleev refers to the "law of periodicity" (zakon periodichnosti) (see below). From this time on, such terms were commonly used by Mendeleev.

attempt in that form in which the matter is now presented.[231] I dare to call the system now proposed a natural system of the elements, because the comparisons made by me concerning a multitude of more or less precisely observed properties - not only of the elements, but also of their various compounds - have shown me that in not a single case do we encounter an essential obstacle to the application of this system to the study of the properties of the elements and their compounds; on the contrary, many of the properties of the elements and their compounds are clarified by this system, and sometimes also given an unexpected simplicity and coherence.[232]

In March 1871 the following statement of, and comment upon, the "law of periodicity" of the chemical elements was published in part II of the 1st edition of Mendeleev's Principles of Chemistry:

> ... a regular and gradual change in the magnitude of the atomic weight entails a regular and gradual change in both the qualitative and the quantitative capacity of the elements for combination,[233] and at the same time there is a periodic repetition of both qualitative and quantitative properties accompanying the gradual increase in atomic weight. This is the deduction from all comparisons which have been made in this respect, and discloses - in my opinion - a new point of view to the elements, although despite all the apparent simplicity of the affair we have as yet no possibility of maintaining any kind of hypothesis which adequately explains the law of periodicity.[234]

Later in the same work Mendeleev states the periodic law as follows: "... the physical and chemical properties of the elements, which are displayed in the properties of the simple and compound bodies which are formed by them, stand in periodic dependence upon (are a periodic function of - to use a mathematical term[235]) their atomic weights".[236] Also in part II of the

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[231] As what we might call a "vertical short-form table" (see later in the present chapter).

[232] J.Russ.Chem.Soc., 1871, pp.25-31; PLBA, 69-75.

[233] By "the qualitative and the quantitative capacity of the elements for combination" Mendeleev presumably means the types of reactions of the elements, and their valencies.

[234] Pr.Ch., R-1, part II (1871) 833-4; PLBA, 380-1.

[235] The "mathematical term" to which Mendeleev is here referring is clearly "function", not "periodic", because the latter term is used also outside the parentheses.

[236] Pr.Ch., R-1, part II (1871) 941 An identical formulation of the periodic law was given in R-2, part II (1873) 920. In R-3 (1877) - the first edition of Pr.Ch. to have a special chapter devoted to the periodic law - we find the following mode of expression (on p.847), which was retained in all of the subsequent editions prepared by Mendeleev: "... if all the elements are arranged according to the magnitude of their atomic weights, then a periodic repetition of properties is obtained. This is expressed by the law of periodicity: the properties of the simple bodies, as well as the forms and properties of the compounds of the elements, are in periodic dependence upon (or, expressing ourselves algebraically, form a periodic function of) the magnitude of the atomic weights of the elements".

1st edition of Principles of Chemistry was included a folding sheet entitled D. Mendeleev's natural system of the elements (R.), which presented tables 31 (P8) and 32 (P9); this sheet had been drawn up in February, 1871.

In about March of 1871 Mendeleev began to prepare a new article on the periodic law, for publication in a German journal. He soon decided to write two such articles, one dealing solely with the question of priority of discovery of the periodic law, and the other dealing with the nature and applications of the law. The article on priority was published in April in Berichte, as Zur Frage über das System der Elemente (On the question of the system of the elements).[237] It contains Mendeleev's first published use of the label "periodic" in referring to his classificatory system of the elements.[238] The second article was completed by Mendeleev in August 1871; he passed it on to F.R. Wreden fro translation into German, Wreden's translation being published in November in Liebig's Annalen as Die periodische Gesetzmässigkeit der chemischen Elemente (The periodic lawfulness of the chemical elements).[239] On an off-print of this article Mendeleev later wrote, "This is the best-known of my articles";[240] and it was indeed probably through this article rather than any other that non-Russian (especially German) chemists became acquainted at first hand with Mendeleev's detailed views on the nature and applications of the periodic law and periodic system.[241]

In December 1871 Mendeleev discontinued his series of laboratory researches - upon which he had been engaged since 1868 - in fields of

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[237] Berichte, 4 (1871) 348-52. Given in Russian translation in PLBA, 386-91. The content of this article is considered in Ch.VIII.

[238] "It would be more correct to call my system 'periodic' [sc. than merely 'natural'], because it arises from the periodic law" (Berichte, p.350; PLBA, 388.

[239] Annalen (Liebig), Suppl. VIII (1871) 133-229; containing tables 35(P11) and 36(P12). The contents of this article are considered in certain other chapters, as appropriate.

[240] See PLBA, 696.

[241] French and English translations of this article were published in the Moniteur Scientifique (1879) and the Chemical News (1879-80) respectively (see Ch.II, n.156), as a result of the interest aroused in Mendeleev's periodic law by the discovery of gallium (1875) and scandium (1879), which had confirmed his predictions of 1870-1 regarding "eka-aluminium" and "eka-boron" (see Ch.VI).

inorganic and physical chemistry closely connected with the emergence and development of his periodic system. He turned now to an experimental investigation of the "elasticity of gases", a subject which was to occupy him until 1881.

In discussing the different types of arrangement to be found in Mendeleev's periodic tables it will be convenient to use various specific descriptive terms. The following distinctions are drawn:-

i) "Long-form"/"short-form"

The description "long-form" periodic table will be used for those tables in which the elements are arranged in "periods", with the elements of each "large period" (or "long period") being presented in a single line, e.g. table 8 (P1), table 35 (P11), table 44 (P19). In "short-form" tables on the other hand the elements are arranged in "series", where the elements which would constitute a single long period in a long-form table are presented instead in two consecutive parallel series, e.g. table 10 (P3), table 36 (P12), table 60 (P33).[242] Thus, whereas in a long-form table the elements K→Br are arranged in a single line (as a long period), in a short-form table these elements are arranged instead in the two consecutive parallel series,

K——→Ni, Cu
(Cu)Zn→Br.

ii) "Vertical"/"horizontal"

Following the convention of Soviet historians of science such as Kedrov, the terms "vertical" and "horizontal" will be used in this thesis to designate periodic tables according to the orientation of the groups (such as the alkali metals, halogens, etc.), not according to the orientation of the periods or series[243], e.g. table 8(P1) would be classed as a horizontal long-form table, table 44(P19) as a vertical long-form table, table 10 (P3) as a horizontal short-form table, and table 36 (P12) as a vertical short-form table.

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[242] The term "series" is used in this sense by Mendoleev himself (Russian, riad).

[243] The opposite designation, where the table is classed as "vertical" or "horizontal" according to the orientation of the periods or series, is used by some, e.g. by Quam and Quam, Bibl. 96. Others appear to use the terms "vertical" and "horizontal" to describe periodic tables without consistently tying these terms to the orientation of the groups, series or periods, but rather according to some general impression of overall shape of the table, e.g. Venable, Bibl.124.

iii) "Linear"/"zig-zag" (for short-form tables)

In short-form tables the elements within a group (composed of two sub-groups) may be arranged either "linearly", such as,

Li Na K Cu Rb Ag Cs (e.g. in table 10),

or in either a "full" or a "partial" "zig-zag" form, such as,

Li K Rb Cs ("full zig-zag", e.g. in table 36),
Na Cu Ag

or,

Li Na Cu Ag ("partial zig-zag", e.g. in table 16).
K Rb Cs

iv) "Upright"/"inverted" (for horizontal tables)

In some of his early manuscript horizontal tables - e.g. table 2 (M2), table 16 (M10) - Mendeleev arranged the elements not in what might be called "upright" form, with the atomic weight increasing in passing down the columns, but rather in an "inverted" form in which the atomic weight increases in going up the columns.

Using this system of terms, we shall now consider certain detailed aspects of the path by which Mendeleev passed from his original "attempt at a system" - table 3 (M3), 17th February (O.S.) 1869 - to his "natural system", table 26 (M19), 29th November (O.S.) 1870.[244]

a) Mendeleev's "doubling-up" of the long columns of the long-form table 3 (M3) to give a short-form table

The first short-form table known to have been drawn up by Mendeleev[245] was the manuscript horizontal table 5 (M5), compiled towards the end of February (O.S.) 1869. The process of transition from Mendeleev's original long-form table, table 3 (M3), to this first short-form table has been schematically represented by Kedrov in a diagram which he calls "a general scheme of the doubling-up of the long rows of 'An attempt at a system of the

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[244] Table 26 (M19) is the manuscript version of table 30 (P7), published in the article A natural system of the elements.

Those aspects of the path by which Mendeleev passed from his "attempt at a system" to his "natural system" which form part of the topics of Chs. V, VI and VII are considered mainly in these later chapters; only those aspects which do not fit naturally into Chs. V, VI and VII are considered in detail in the present chapter.

In the following discussion a great debt is owed to Kedrov's survey article The development by D.I. Mendeleev of a natural ("short") system of the elements (R.) in Sc.Ar. (pp. 771-858), and indeed to Kedrov's comments throughout Sc.Ar.

[245] Excluding any embryonic short-form tables which he may have constructed on Feb. 17th (O.S.) 1869, such as the lower part of table 1 (M1). On the possibility of Mendeleev's construction of an embryonic vertical short-form table on the morning of Feb. 17th (O.S.) 1869, see n.253, below.

elements'"[246] (see Fig. III-17, below). Kedrov provides the following explanatory note with this scheme:

> The light print ... designates elements which did not undergo transfer and remained in their previous places; they constitute the entire central part of the previous long table ... The heavy print designates elements which underwent transfer from the lower or upper parts of the table (i.e. from its edges) into its centre; the arrows indicate the direction of this transfer. The eight elements which were temporarily excluded from consideration have been isolated ... by broken lines.[247]

Various points may be noted in connection with the transition from table 3 (M3) to table 5 (M5):-

i) The 8 elements, H, Er, Yt, In, Ce, La, Di and Th were included in table 3 (M3), but are omitted from table 5 (M5). Apart from H, these are elements whose atomic weights and chemical characteristics were at the time not known with any certainty.[248]

ii) The transfer of the elements Li, Na, K, Rb, Cs, Ca, Sr and Ba from the lower part of table 3 (M3) to the upper part of table 5 (M5) meant that the halogens and alkali metals were no longer juxtaposed, thus already removing one of the defects of his Attempt at a system which Mendeleev acknowledged in Correlation of properties.

iii) The transfer of Li and Na to the top of the table removed the grounds for postulating the existence of the unknown elements ? = 8 and ? = 22 which Mendeleev had included between H and Cu in table 3 (M3).

iv) Table 5 (M5) contained two empty places between V and Cr, and two between Nb and Mo, which are not to be found in table 3 (M3). Of these four new places, only one is actually that of an unknown element (Tc); the other three are the rightful places of Cr, Mn and Mo, these elements being incorrectly listed in table 5 (M5) with the iron and palladium elements.[249]

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[246] Sc.Ar., 776.

[247] Ibid., 777

[248] Di turned out to be not a single element, but a mixture of two elements, Nd and Pr (von Welsbach, 1885); Mendeleev's "Er" of 1869 contained, in addition to the modern element Er, also the elements Yb, Lu, Ho, Tm and Dy.

In, Ce and Th came to be confidently placed by Mendeleev in his "natural system", table 26 (M19); Yt was tentatively placed; and Er, La and Di were unplaced, although they had been tentatively placed in a number of different ways in various earlier tables of 1870. (See Chs. VI and VII).

[249] The criterion used here and elsewhere in this thesis for assessing the correctness of the placing of elements in Mendeleev's periodic tables is that of correspondence, with respect to sequence of arrangement and group-membership, to the placing of elements in the modern periodic table.

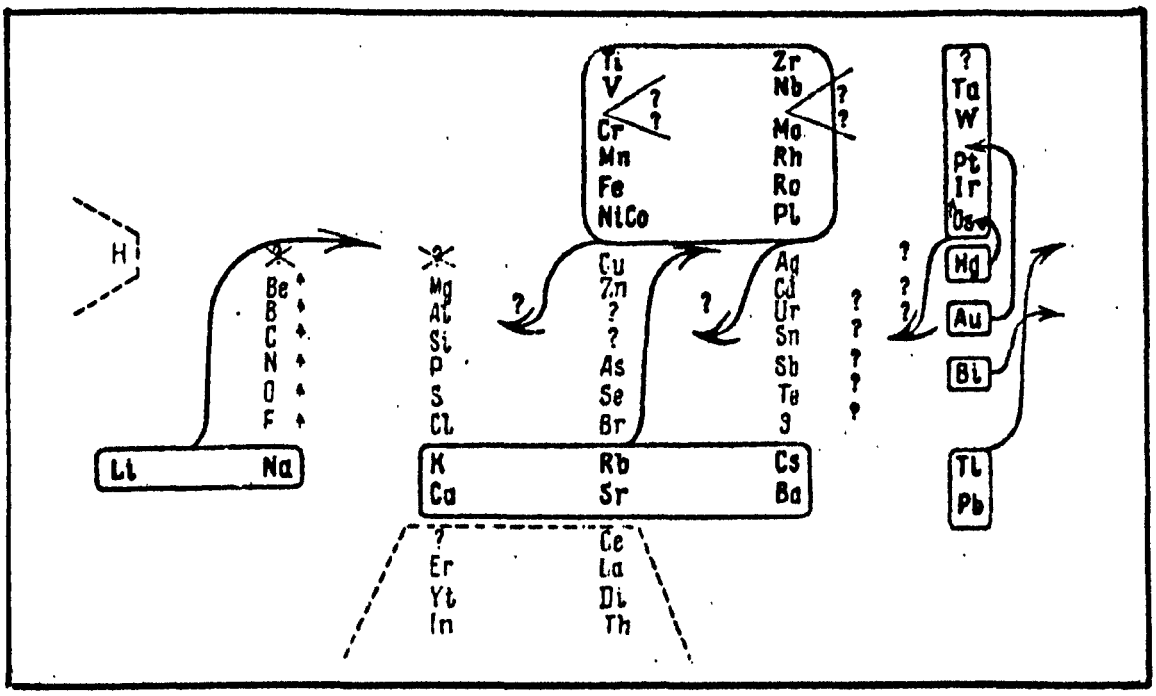

Fig.III-17 (Kedrov).

v) In going from table 3 (M3) to table 5 (M5) the atomic-weight value of Te has been changed from 128? to 125, not on empirical grounds but solely to accord with the placing of Te between Sb = 122 and I = 127.

vi) The doubling-up of the long columns of table 3 (M3) to give table 5 (M5) produced the advantage of indicating the analogies between the different sub-groups within a group, e.g. the analogies between the sub-group containing Ca, Sr and Ba, and that containing Zn and Cd.[250] The existence also of significant differences between the properties of the different sub-groups of a given group is represented in table 5 (M5) by the use of a zig-zag arrangement, e.g. $Ca_{Zn}Sr_{Cd}Ba$.

Although Mendeleev presented the horizontal long-form table 9 (P2), which was based upon table 3 (M3), as the central system in his article Correlation of properties, this article also reflects Mendeleev's attempts at doubling-up the long columns of table 3 (M3) to give a horizontal short-frm table. Table 10 (P3), given in a footnote in this article, is a horizontal short-form table which is clearly based upon the earlier table 5 (M5), even though table 10 (P3) has a linear form while table 5 (M5) has a zig-zag form.[251] Later in Correlation of properties Mendeleev discussed at some length the relative merits of a linear short-form table such as table 10 (P3) and a long-form table such as table 9 (P2), preferring on balance the latter form of presentation: he felt that the advantage of the linear short-form table in expressing the analogies between the sub-groups within a group was outweighed by the disadvantage of this table in disturbing the juxtaposition of the most closely analogous elements (i.e. of the elements of the same sub-group) which is to be found in the long-form table.[252] Why Mendeleev did not here suggest the zig-zag short-form arrangement as a possible compromise solution is somewhat strange, since he had already drawn up such a presentation in table 5 (M5).

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[250] Kedrov (Sc.Ar., 784) refers to the existence of resemblances between the sub-groups of a group as providing "a real basis for the doubling-up of the rows in the short table".

[251] That table 10 (P3) is based upon the earlier table 5 (M5) is clear from the fact that table 10 (P3), like table 5 (M5), contains gaps corresponding to the places where Cr, Mn and Mo should be.

[252] Op.Cit., pp. 71-2; PLBA, 24-7.

b) The transition by Mendeleev from a horizontal short-form table to a vertical short-form table

Very soon after compiling the horizontal short-form table 5 (M5), Mendeleev (late Feb., O.S., 1869) drew up table 6 (M6), which is the earliest known example of a vertical short-form table constructed by him.[253] The following points may be noted in connection with the transition from table 5 (M5) to table 6 (M6):-

i) Of the 8 elements H, Er, Yt, In, Ce, La, Di and Th omitted from table 5 (M5), only H is included in table 6 (M6), in the middle of the otherwise empty row above the Li-F row (i.e. approximately above C). The remaining 7 of these elements are listed at the bottom of the sheet on which table 6 (M6) is drawn up, but outside the table itself.

ii) Unlike table 5 (M5), which had Cr, Mn and Mo erroneously placed with the iron and palladium elements (leaving gaps corresponding to their correct places), table 6 (M6) has these elements placed correctly. But not only Cr, Mn and Mo have been moved from the "group VIII" region[254] of table 5 (M5) to the main body of the table in table 6 (M6); in the latter table Mendeleev has put rhodium ("Ro") and platinum into the column containing the halogens and manganese (into the places corresponding to technetium and rhenium respectively).

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[253] Although most of the references to short-form arrangements of the elements in Mendeleev's article Correlation of properties concern horizontal arrangements, there is one passage, fairly early in the article (op.cit., p.67; PLBA, 18), where Mendeleev presents a partial vertical short-form arrangement, and appears to suggest that such an arrangement of the elements represented the first stage ("first trial", pervaia proba) in his construction of the periodic system. Perhaps this was indeed so, in which case this embryonic vertical short-form arrangement would presumably have been drawn up by Mendeleev on the morning of February 17th (O.S.) 1869 (judging from Kedrov's account of the history of Mendeleev's discovery of the periodic law, given in Bibl. 44), before he drew up the partial horizontal arrangement presented in Ch. IV as table 1 (M1). There is, however, no supporting evidence for such a suggestion, which on the contrary seems rather unlikely since all of the known manuscript tables drawn up by Mendeleev on Feb. 17th (O.S.) 1869 are of the horizontal type. It seems more likely that this passage from Correlation of properties where Mendeleev talks of his "first trial" at drawing up a system of the elements on the basis of atomic weight is not historically accurate as regards the structural details (orientation, compactness) of his actual "first trial".

[254] This is a convenient anachronistic use of the term "group VIII", a term introduced by Mendeleev towards the end of 1870 (see later in the present chapter).

iii) Mendeleev had difficulty placing Hg, Au and Bi in table 6 (M6). He at first placed Hg = 200 at the foot of the column containing F, Cl, Mn, etc., but then wrote "the position of this is wrong", and crossed it out; he ends up placing Hg, together with Au = 197, slightly off the table to the left of Tl = 204 (which is at the foot of the column containing Li, Na, K, etc.). Au is given an alternative place at the base of the column containing B, Al, etc. Also at the foot of the B - Al column, just above Au 197, is the entry Bi = 200, with the note "an analogue of boron??". A second place suggested for Bi is at the foot of the N - P column, where we find the entry Bi?. The placing of Au at the foot of the B - Al column is presumably conditional upon placing Bi in the N - P column.

iv) Unlike table 5 (M5), which had a zig-zag arrangement of elements within the groups, table 6 (M6) has a linear arrangement. In table 6 (M6) Mendeleev seems to attempt to indicate the different sub-groups instead by marking the alternate rows "//" or "\\" according to the particular sub-group to which the members of the row belong: thus, the rose Li - F, K - Mn, Rb - Ro, etc., are marked "//", and the rows Na - Cl, Cu - Br, Ag - I, etc., are marked "\\". It appears, however, that Mendeleev encountered a problem in connection with the marking of the row containing Ta and W. These two elements are closely analogous to Nb and Mo respectively, showing much less analogy to Sb and Te; but the sequence of rows in table 6 (M6) suggests that Ta and W belong to the same sub-groups as Sb and Te, not Nb and Mo.[255] Both types of mark, "//" and "\\", are found in the Ta - W row in table 6 (M6): the mark "//" is that required by the close resemblance of the elements of this row to those of the Rb - Ro row, whereas "\\" is demanded by the symmetry of table 6 (M6). As has been suggested by Kedrov,[256] the interest shown by Mendeleev in the atomic-weight values which would be required for the (unknown) elements corresponding to the gaps between Ba (= 137) and Ta (= 182) in table 6 (M6) was probably provoked by the thought (arising out of the problem of marking the Ta - W row in this table) that perhaps there is an extra row, as yet completely empty, between the Cs - Ba row and the Ra - W row. With such an extra row, the symmetry of the table would be more favourable to marking the Ta - W row "//"[257], in accordance with the

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[255] The zig-zag arrangement of table 5 (M5) also had Ta and W in the wrong sub-groups, but there are no signs that Mendeleev had been disturbed by this fact in this earlier table.

[256] Sc.Ar., 61.

[257] The symmetry would still not be completely favourable in such a case because of the problem of Pb, mentioned below.

requirements of chemical analogy. However, a consideration based merely upon the atomic-weight differences in the region between Ba and Ta turns out to be somewhat inconclusive for a judgment on the question of the possible existence of an extra row between the Cs - Ba and Ta - W rows.[258] The major factor in discouraging Mendeleev's introduction of such an extra row into table 6 (M6) was probably his misplacing in the table of Pb with the alkaline-earth elements.[259] With Pb listed as an analogue of Ca, Sr and Ba, the mark "//" which Mendeleev had given to the Pb - Bi row would seem quite natural; and with the Pb - Bi row marked thus, the introduction of a new row between the Cs - Ba and Ta - W rows would require the introduction also of a new row between the Ta - W and Pb - Bi rows, an extension completely unjustified on grounds of atomic-weight difference.[260] Mendeleev seems in table 6 (M6) to have reluctantly accepted Ta and W as members of the sub-groups containing Sb and Te respectively: beneath W in this table he wrote, "must represent an analogue of S, Se, Te", and of the 5 marks (four "//", one "\\") which he had placed in the Ta - W row, he crossed out 2 of the "//" marks.

Some time during the period March-June 1869 Mendeleev drew up another vertical short-form table, table 11 (M8). Apart from the fact that this new table was linear and vertical, whereas table 5 (M5) was zig-zag and horizontal, table 11 (M8) was very similar to table 5 (M5), showing a lesser similarity to the previous vertical table, table 6 (M6). Among the characteristics of table 11 (M8) may be noted the following:-

i) H is placed in table 11 (M8) in roughly the same position as in table 6 (M6), viz. in the middle of the otherwise empty row above the Li - F row.

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[258] Assuming the Cs-Ba and Ta-W rows to be adjacent in the vertical short-form table, the average atomic-weight difference between consecutive (unknown) elements in the region between Ba and Ta would be about 4.5 atomic-weight units, which although somewhat higher than the average difference for consecutive elements in the other rows is not so high as to be definitely unacceptable.

[259] Mendeleev had listed Pb as an analogue of Ca, Sr and Ba also in table 3 (M3).

[260] The other possibility open in principle, that of placing Ta and W in the same row as Cs and Ba, is quite unacceptable not only on the grounds of the atomic-weight difference between Ba and Ta (although see table 15 in Ch. IV, discussed in Ch. VI), but also on the grounds that with Pb taken as an analogue of Ca, Sr and Ba this would still require an additional row between the Ta-W row and the Pb-Bi row.

Later, when Pb was correctly classified as an analogue of Sn, Mendeleev could introduce a new row between the Cs - Ba row and the Ta - W row, and indeed did so (in 1870 - see later in the present chapter).

ii) Cr, Mn and Mo are placed in table 11 (M8) with the iron and palladium elements, as in table 5 (M5) but unlike table 6 (M6); as in table 5 (M5), the proper places of Cr, Mn and Mo are vacant. Also vacant in table 11 (M8) are the places corresponding to Tc and Re - again, like table 5 (M5) but unlike table 6 (M6).

iii) As in table 5 (M5), but unlike table 6 (M6), the elements Hg and Au are placed in table 11 (M8) in association with the platinum metals (in what later came to be called "group VIII"). However, the arrangement of elements within this enlarged platinum family is rather different in the two tables 5 (M5) and 11 (M8), over and above the difference arising merely from the different orientations of these tables, viz.

table 5 (M5):		table 11 (M8):			
	Au		Pt	Ir	Os
	Pt		Hg		Au
Os	Ir				
	Hg				

iv) Unlike either table 5(M5) or table 6 (M6), in table 11 (M8) an attempt is made to include the elements In and Ce, based upon the assumption of the (incorrect) atomic-weight values In = 75.6 and Ce = 92. Indium is listed between Zn and Sr;[261] and cerium is placed with the palladium family, thus - Mo Rh Ru Pl .
Ce

After May 1869, when the horizontal short-form table 10 (P3) was published, the short-form tables published by Mendeleev (such as his "natural system") were all of the vertical type. However, we do find the occasional horizontal short-form table in manuscript after this date, e.g. tables 16(M10) and 17 (M11), dating from 1870.

c) The emergence of a co-ordinate system for the short-form periodic table through Mendeleev's introduction of numeration of the groups and series

Mendeleev seems not to have begun to introduce actual numeration of the rows and columns of his periodic system until the summer - early autumn of 1870.[262] However, a precursory stage to his numbering of the groups (i.e. of

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[261] There is no proper place in the table to correspond to such a placing of In between Zn and Sr; in table 11 (M8) In is merely included between rows. In Correlation of properties (op.cit., p.72; PLBA 26) Mendeleev suggested that perhaps In = 75.6? be inserted (in a short-form arrangement) between Zn and Cd, presumably instead of Sr. Perhaps it is this idea that Mendeleev is expressing in table 11 (M8).

[262] Mendeleev's first use of such numeration was in manuscript periodic systems. His earliest published table with numeration was table 30 (P7), published Feb. 1871. Earlier numeration of either groups of series by other contributors may be seen in Figs. III-2 (Newlands, 1864; numeration of groups), III-13 (Meyer, 1868; groups), III-11 (Hinrichs, 1869; series) and III-14 (Meyer, 1870; series). In 1872 (Fig. III-16) Meyer numbered only the series.

the columns in the vertical type of table, of the horizontal rows in the horizontal type of table) may be seen in his characterisation of the various groups by the form of "saline" oxide in which the elements of the group show their highest valency.[263] In his first article on periodicity - Correlation of properties - Mendeleev had remarked, "The arrangement of the elements or their groups according to atomic weight corresponds to their so-called atomicity",[264] but here he is referring to the usual valency of the elements, as manifested in their hydrogen or chlorine compounds.[265] Similarly, in his article Atomic volumes Mendeleev said: "... the system [sc. the vertical short-form table 14 (P5)]... corresponds to the atomicity of the elements as it is usually recognised; thus, the elements of the first column are monoatomic, and of the second, third and fourth are di-, tri- and tetra-atomic; the elements of the fifth column are triatomic, of the sixth column, diatomic, and of the seventh column, monoatomic".[266] In this same article, however, he also said: "... while being based upon the magnitude of atomic weight, such a system graphically expresses chemical similarity, it defines the degree of combination with oxygen".[267] This is the first time that Mendeleev had

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[263] Kedrov (Sc.Ar., 797) has written: "... D.I. [Mendeleev] did not introduce ... [numeration of the groups and series] ... until a real physical or chemical significance was found for those numbers which had to serve as the numbers of the groups or the numbers of the series. The necessity for numeration of the series in the short table followed from the alternation of full analogues and incomplete analogues in the short table of the elements; numeration of the groups was a direct consequence of the establishment of the maximum valency of the elements of a given group with respect to oxygen". While the opinion expressed here by Kedrov concerning the basis for the numeration of the groups is largely echoed in this thesis, his comment on the basis of numeration of the series seems rather to exaggerate the significance of the alternation of the sub-groups. Numeration of the series certainly led to Mendeleev's "even"/"odd" distinction between the alternating sub-groups of a group (see below), and in this and other respects is convenient; but the mere fact of the alternation of the sub-groups can hardly be considered as leading directly to the need for numeration of the series.

Certain weaknesses in Mendeleev's distinction between "saline" oxides and "peroxides" are discussed in Ch. V.

[264] Op.cit., p.76; PLBA, 30.

[265] See Correlation of properties, pp. 68-9; PLBA, 20-1.

[266] Op.cit., p.63; PLBA, 33.

[267] Ibid.

distinguished between the significance of the periodic system in connection with the usual valency of the elements, and with their valency with respect to oxygen. Later in the article he talked about the analogies between Cr and S, and between Mn and Cl, in their highest oxidation states, i.e. between So_2Cl_2 and CrO_2Cl_2, and between $KMnO_4$ and $KClO_4$.[268] Shortly afterwards (Oct. 1869), in his paper On the quantity of oxygen, Mendeleev introduced more explicitly the idea of characterising the groups in his periodic system by means of the forms of saline oxide in which they show their highest valency. At this stage he talked about only the first 7 groups in his (short-form) periodic system:

> ... we are confronted with only 7 limiting forms of saline oxide. These forms ... may be expressed as,
>
> R_2O; R_2O_2; R_2O_3; R_2O_4; R_2O_5; R_2O_6; R_2O_7.
>
> To this series correspond exactly those 7 series of simple bodies [sc. the "groups"] into which it is most natural to distribute the majority of the elements which have been grouped according to similarity of properties and according to the periodicity which has been determined in their atomic weights.[269]

A little later in the same article Mendeleev wrote, referring to table 13 (P4), "The naturalness of this grouping is amplified by the fact that it is shown to comply with that order in which the elements are distributed according to the form of their limiting saline oxides".[270] This correspondence which Mendeleev had now recognised between the order of the groups in the periodic system and the maximum valency of the elements in their saline oxides was presumably what he had in mind when in 1870 he wrote that his "natural system of the elements" provided "a new explanation of the so-called atomicity of the elements".[271]

It was not until the late autumn of 1870 that Mendeleev came to extend the correlation of position in the periodic system with composition of the highest saline oxide to the group containing the elements of the iron, palladium and platinum families. But by this time he had already begun to introduce numeration of the rows and columns of his periodic table.

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[268] Op.cit., p.63; PLBA, 34.

[269] Op.cit., pp. 15-16; PLBA, 52.

[270] Op.cit., pp. 16-17; PLBA, 53. Again, later in this article Mendeleev presented the conclusion quoted earlier in the present chapter on p.171.

[271] On the place of cerium (G.), p.49; PLBA, 67.

The earliest periodic table of Mendeleev's known to contain numeration of rows or columns is the inverted horizontal short-form table 16 (M10), dating from the summer - early autumn of 1870. In this table the first five columns after the Li - F column are labelled by means of Arabic numerals - 1, 2, 3, 4 and 5. In the horizontal short-form table 17 (M11), compiled very soon after table 16 (M10), numeration of the columns was extended to the 6th column after the (un-labelled) Li - F column, i.e. the column containing Cs and Ba was labelled "6". Also in table 17 (M11), Th (= 231) and U (= 240) were for the first time listed as the heaviest elements, creating a new column (corresponding to a new horizontal row in a vertical table) at the "heavy" end of the periodic system.

Shortly afterwards, still in the summer - early autumn of 1870, Mendeleev first introduced numeration of the groups, in the horizontal long-form table 18 (M12). He used a mixture of Roman and Arabic numerals for this purpose (viz. I, II, III, 4, 5, 6, 7). There was no numeration of the columns in this table.[272]

In the vertical short-form table 19 (M13), dating from the same period, Mendeleev introduced an extra (completely empty) row between the Cs - Ba and Ta - W rows. All of the rows of his "natural system" had now been introduced. Table 19 (M13) had no numeration of rows or columns.

In the autumn of 1870, in a manuscript rough draft of his proposed article Towards a system of the elements (R.),[273] Mendeleev for the first time referred to the places of the elements within the periodic system by means of two co-ordinates, taken from the numeration of rows and columns in the vertical short-form table 20 (M14) which accompanied this manuscript draft. In table 20 (M14) the groups were numbered using the Roman numerals I-VII (the elements of the iron, palladium and platinum families were not included in the table), and the rows numbered using the Arabic numerals 0, 1, 2, ... 8, from the Li - F row to the Ta - W row.[274] The places in

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[272] Since table 18(M12) is long-form, the columns in this table correspond to periods, not to series.

[273] Not published under this title (see earlier).

[274] This is Mendeleev's first use of the numeral "0" to designate the Li - F row. He very soon discarded this designation (see below).

Table 20 (M14) does not contain H; and although it has a row containing only Th = 231 at the bottom of the table, and also a horizontal line between this row and the Ta - W row, corresponding to the Hg - Tl row, there is no numeration of rows beyond the Ta - W row.

table 20 (M14) were referred to in the text of this manuscript rough draft of Towards a system of the elements with the Roman numeral (the number of the group) given first, e.g. the places of Sr, Ba, Rb and Cs were referred to as (II-4), (II-6), (I-4) and (I-6) respectively.[275] This mode of designation of the places in the short-form periodic table was retained by Mendeleev throughout his life, although the particular system of numeration of the groups was changed by him in 1871 (see below).

By early November 1870 Mendeleev had written his third (and final) manuscript draft of Towards a system of the elements.[276] In this manuscript he retained the designation "0" for the Li - F series. In the vertical short-form table 23 (M16) drawn up very soon afterwards (early November) he had already discarded this "0" designation of the Li - F series, and did not use it again.[277] In table 23 (M16) the Li - F series is not labelled in any way at all. Numeration in this table extends for the first time to series 10 (i.e. to the Th - U series, the Na - Mg series being series 1); also for the first time the elements of the iron, palladium and platinum families are labelled "group VIII". The list of characteristic highest saline oxides included in table 23 (M16) gives the type "RO_4" for group VIII.[278] That Mendeleev now came to recognise the existence of oxides of the form RO_4 for this group - and consequently to designate it "group VIII" - almost certainly arose out of his work at this time in preparing the chapter in Principles of Chemistry (part II, Ch.XIX) which deals with the palladium and platinum metals.[279] In this chapter Mendeleev wrote:

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[275] See Sc.Ar., 123.

[276] See Sc.Ar., 132-7.

[277] The designation "0" for the Li - F series was therefore never used by Mendeleev in a published work. Much later, in the early 20th century, Mendeleev again introduced the designation "0" into the numeration of the series, this time to denote the "pre-hydrogen" series in which he placed the hypothetical element x (tentatively identified with the ether).

[278] Table 23 (M16) seems to be the earliest full periodic table to include the forms of the highest saline oxides characteristic of the groups, and also the first to give the characteristic hydrides. However, certain of Mendeleev's earlier partial tables already include these features, e.g. that given in Sc.Ar., 132 (from the 3rd draft of Towards a system of the elements, early Nov. 1870).

[279] This recognition did not come from any original experimental research on these oxides by Mendeleev himself, but rather from his study of the earlier contributions of Tennant, Vauquelin, Berzelius, Wöhler, Fritzsche, Struve and Deville (see Pr.Ch., R-1, part II, 1871, p.833; PLBA, 380).

... ruthenium and osmium ... are able to give ... oxides of the form RuO_4 and OsO_4...

In connection with this form of oxidation RO_4 it should above all be noted that it is the highest of the known forms. If we arrange the elements into groups - as is done at the beginning of this volume [sc. in table 31 (P8)] - we see that according to the sequence of the distribution of the elements the highest form of oxidation, and furthermore the very composition RO_4, should be manifested in the elements of group VIII.[280]

In table 23 (M16) Mendeleev had therefore arrived at the system of numeration which he uses in his "natural system" of elements, table 26 (M19)/30(P7).[281] Although in tables 24 (M17), 25 (M18) and 26 (M19) Mendeleev does not designate the Li - F series by a number, he does now label it "typical series" ("typical row") or "typical elements".[282]

Mendeleev's numbering of the series in his short-form periodic table led him to introduce the terms "even" (chetnyi) and "odd" (or "uneven", nechetnyi) to denote series labelled by an even or odd number respectively. The elements of a given group belonging to the even series represent one sub-group of this group, and the elements belonging to the odd series, the other sub-group.[283] Because the elements coming before Na in Mendeleev's "natural system" table 30 (P7) (the so-called "typical" elements) were given no series-number, they were not at the time designated as "even" or "odd". For the same reason, the co-ordinate system for labelling the places in Mendeleev's short-form table did not in table 30 (P7) encompass the places of the elements coming before Na.

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[280] Pr.Ch., R-1, part II (1871) 832-3; PLBA, 379-80.

[281] Table 30 (P7) was the first published table of Mendeleev's to contain any numeration of groups and series.

[282] Table 24 (M17) is a rough draft of the table published as table 33(P10); table 25 (M18) is the manuscript fair-copy of table 24 (M17). On the significance of Mendeleev's use of the term "typical" to denote the lightest elements, see n.205 of the present chapter. Mendeleev showed a certain inconstancy as regards the particular elements he called "typical": at first he referred only to the elements H, Li ... F as "typical" (e.g. in tables 30, 33, 35); soon he tended to include also Na (e.g. in tables 45, 47), and sometimes both Na and Mg (see, for example, PLBA, 118 - from his 1871 Annalen paper); much later in his life he even occasionally included all elements up to argon (tables 57, 63).

[283] On Mendeleev's distinction between "even" and "odd" series according to ability to form organometallic compounds and volatile hydrides, see Ch.V. Mendeleev later distinguished the "even" and "odd" series also according to the magnetic properties of the simple substances ("even" series - paramagnetic; "odd" series - diamagnetic), acknowledging in this respect the work of Errera (Belgium, 1878) and Carnelley (England, 1879) (e.g. see PLBA, 299: from Pr.Ch., R-8, 1906).

By the second half of 1871 Mendeleev had modified his scheme of numeration of the series in the short-form table, introducing in table 36 (P12) the numeration 1 - 12, where series 1 contains only H, series 2 contains Li - F, and series 3 - 12 are those series which had been labelled 1 - 10 in his original "natural system", table 30 (P7).[284] This change introduced the "typical" elements into the scheme of classification of the series as "even" or "odd"[285]; it did not, however, alter the classification in this respect of the other series, since it resulted merely in their series-numbers being increased in value by 2. Mendeleev's modified system of numeration of the series also now enabled every place in the short-form periodic table to be conveniently denoted by means of two co-ordinates. This new system of numeration presented in table 36 (P12) was retained by Mendeleev throughout his life (it was, however, extended by him in the early 20th century, in connection with the placing of the inert gases in the periodic table and with his "chemical conception" of the ether, to include also a "zero" group and "zero" series).[286]

d) The changes in the classification by Mendeleev during the course of the transition from his original "attempt at a system" to his "natural system" of certain elements whose accepted atomic-weight values remained more or less constant during this period: H, Au, Hg, Tl, Pb, Bi, and the elements of the iron, palladium and platinum families.[287]

The three charts given below illustrate the changes in classification by Mendeleev, during the course of his transition from table 3 (M3) to table 26 (M19), of H (Fig. III - 18), Au, Hg, Tl, Pb and Bi (Fig. III - 19), and the elements of the iron, palladium and platinum families (Fig. III - 20).[288]

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[284] Table 36 (P12) accompanied Mendeleev's Annalen paper of 1871.

[285] Series 1 (containing only H) being "odd", series 2 (Li - F) being "even". Mendeleev still retained the label "typical" for the lightest elements (see n.282, above).

[286] Where the position of an element in the short-form periodic system is denoted in this thesis by means of two co-ordinates, it may be assumed that the co-ordinate system used is Mendeleev's later (complete) system unless some indication is given to the contrary.

[287] Subsequently Mendeleev was to suggest, on the basis of a consideration of position in the periodic table, that the accepted sequence of atomic-weight values for Os, Ir, Pt and Au is wrong, and that perhaps the order of values for Co and Ni is wrong (see Ch. VI).

[288] A chart by Kedrov illustrating these (and other) changes in classification by Mendeleev is given in Sc.Ar., 44-5.

All of the reproduced sections of periodic table are given in the same (vertical) orientation for convenience in making comparisons, although in a number of the original tables the orientation was in fact horizontal. In the sections of table presented in Fig. III - 20 Mendeleev uses the symbol "Pl" throughout for palladium[289]; in tables 3 (M3) and 5 (M5) he uses "Ro" for rhodium, and "Rh" for ruthenium; in table 6 (M6) he still uses "Ro" for rhodium, but now has "Ru" for ruthenium; in the later tables he uses "Rh" for rhodium, and "Ru" for ruthenium.[290]

In his Correlation of properties (1869) Mendeleev had made the following remark concerning the problem of placing H in his "attempt at a system": "Hydrogen, with its small atomic weight, has not found a definite position [sc. in table 9 (P2)]; it seems to me the most natural to place it in the row of copper, silver and mercury, although perhaps its place is in some unknown row below the copper row".[291] Nearly two and a half years later, in connection with his discussion of table 36 (P12) in his article in Liebig's Annalen on The periodic lawfulness of the chemical elements (G.), Mendeleev expressed a more definite opinion on the placing of H, one which he was to retain throughout the remainder of his life:

> The isolated, independent position of hydrogen, with the lowest atomic weight, becomes clear. Because its saline oxide is H_2O, and its salts are HX, it must be included in group I; and its closest analogue will be Na, because this element, like hydrogen, belongs to an odd series in group I. Its further analogues will be Cu, Ag and Au. All five give the corresponding compounds RO and R_2O_2.[292]

The place given to H in table 36 (P12) and later tables is that which was already given in Mendeleev's original "natural system", table 26 (M19)/ 30 (P7). The uncertainty which had been expressed by Mendeleev in

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[289] Although table 26 (M19) has "Pl", the published version of this table, table 30 (P7), has "Pd". Mendeleev changed from "Pl" to "Pd" in late 1870-early 1871.

[290] On the question of the symbols used by Mendeleev in 1869 for ruthenium and rhodium, see Kedrov, Sc.Ar., 39, 43, 44.

[291] Op.cit., p.75; PLBA, 29.

[292] Op.cit. (1871), p.154; PLBA, 118. Some additional analogies between H and the group Na, Cu, Ag, Au were given in the subsequent pages of the article.

Table 3 (M3)- 'attempt at a system'	H ✳ Li Be B C N O F Na Mg ---------- K Cu Zn ---------- Rb
Table 5 (M5)	X
Table 6 (M6)	H Li Be B C N O F
Table 11 (M8)	H Li Be B C N O F
Table 12 (M9)	X
Table 16 (M10)	X
Table 17 (M11)	H Li Be B C N O F Na ---------- K ---------- Fe Co Ni Cu ----------
Table 18 (M12)	H Li Be B C N O F Na ---------- Fe Co Ni Cu ----------
Table 19 (M13)	H Li Be B C N O F Na ---------- K ----------
Table 23 (M16)	X
Table 24 (M17)	✳ H ✳ Li Be B C N O F Na Na ---------- Cl K ---------- Fe Co Ni
Table 25 (M18)	H Li Be B C N O F Na ----------Cl K ---------- Fe Co Ni
Table 26 (M19)- 'natural system'	H Li Be B C N O F Na ---------- K ----------

Fig.III-18.

The placing of H.

Table 3 (M3) – 'attempt at a system'	---Cu Zn ? ? As Se Br Rb Sr--- ---Ag Cd Ur Sn Sb Te J Cs Ba ---Hg – Au – Bi – – Tl Pb
Table 5 (M5)	Ag Cd Ur Sn Sb Te J Cs Ba ? [?] ? ? ? ? ? ? ? Ta W ? Au Pt Os,Ir Hg Tl Pb Bi
Table 6 (M6)	Cs Ba ——————— ? ? ? ? ? Ta W Pt Ir,Os Hg Au Tl Pb Bi Au —— Bi? ~~Hg~~ ———
Table 11 (M8)	Cs Ba – – – – – – – – – Ta W – Pt Ir Os Hg Au Tl Pb Bi – – – –
Table 12 (M9)	Rh Ru Pl Ag Cd – Sn Sb Te J Pt Ir Os Au Hg Tl Pb Bi – –
Table 16 (M10)	
Table 17 (M11)	Ag Cd In Sn Sb Au Hg Tl Pb Bi
Table 18 (M12)	Ag Cd ? Sn Sb Au Hg Tl Pb Bi
Table 19 (M13)	Ag Cd In Sn Sb Au Hg Tl Pb Bi
Table 23 (M16)	(Ag) Cd In Sn Sb Te J – – – Os Ir Pt Au (Au) Hg Tl Pb Bi – –
Table 24 (M17)	Ag Cd In Sn Sb Te J Os Ir Pt [Au?] [Au?] Hg Tl Pb Bi – –
Table 25 (M18)	[Ag] Cd In Sn Sb Te J Os Ir Pt Au [Au] Hg Tl Pb Bi – –
Table 26 (M19) – 'natural system'	[Ag] Cd In Sn Sb Te J ——— Os Ir Pt Au [Au] Hg Tl Pb Bi – –

Fig. III-19.

The placing of the elements Au, Hg, Tl, Pb and Bi.

Table 3 (M3)– 'attempt at a system'	Cr Mn Fe Ni=Co Cu Mo Rh Ro Pl Ag W Pt Ir Os Hg
Table 5 (M5)	V ? ? Cr Mn Fe NiCo Nb ? ? Mo Rh Ro Pl Ta W ? Au Pt Os=Ir Hg
Table 6 (M6)	Mn Fe Ni Co Br Ro ~~Rq~~ Ru Pl J Pt Ir=Os
Table 11 (M8)	? | Cr Mn Fe Ni Co Br ? | Mo Rh Ru Pl Ce J = Pt Ir Os Hg Au
Table 12 (M9)	Fe Ni Co Cu Zn--- Rh Ru Pl Ag Cd --- Pt Ir Os Au Hg---
Table 16 (M10)	Fe Co Ni Cu Zn--- Pl Rh Ru Ag Cd--- Pt Ir Os --------
Table 17 (M11)	Fe Co Ni Cu Zn--- Pl Ru? Rh Ag Cd--- Os Ir Pt Au Hg---
Table 18 (M12)	Fe Co Ni Cu Zn--- Ru Pl Rh Ag Cd--- Pt Ir Os Au Hg---
Table 19 (M13)	Mn Fe NiCo – Br Rh Ru Pl – J – – – Pt–Os
Table 23 (M16)	Mn Fe Co Ni Cu – Br Ru Rh Pl Ag – J – – – – – – – Os Ir Pt Au
Table 24 (M17)	Mn Fe Co Ni [Cu?] – Br Ru Rh Pl – J [Ce? La? Di? Er?] – – – Os Ir Pt [Au?]
Table 25 (M18)	Mn Fe Co Ni Cu – Br Ru Rh Pl Ag – J [La? Di? Er?] – – – Os Ir Pt Au
Table 26 (M19)– 'natural system'	Mn Fe Co Ni Cu – Br Ru Rh Pl Ag – J – – ——— – Os Ir Pt Au

Fig. III-20.

The placing of the elements of the iron, palladium and platinum families.

Correlation of properties concerning the position of H is however clearly seen (from Fig. III - 18) to have persisted throughout the period from the time of his compilation of table 3 (M3) to the time when he eventually drew up table 26 (M19); even in table 25 (M18) he had listed H not in group I, but in group VIII instead.[293]

As regards the placing by Mendeleev of Au, Hg, Tl, Pb and Bi, all these elements had been placed correctly by June (O.S.) 1869, in table 12 (M9). With these elements correctly placed Mendeleev was now free to introduce an extra (completely empty) row between the Cs - Ba and Ta - W rows of the short-form table.[294] However, such a new row was not introduced by Mendeleev until the summer - early autumn of 1870, in table 19 (M13).

On the question of the position in the periodic table of the elements of the iron, palladium and platinum families, Mendeleev had the following to say in Correlation of properties: "A multitude of questions arise in connection with the placing of all of the elements into a single integral system, but the most interesting question seems to me to be the distribution of those elements which resemble iron, cerium, palladium and platinum, because here we have elements which resemble each other in their natures and which also have atomic weights which are close ...".[295] It was not until November 1870, in table 23 (M16), that Mendeleev placed all of the elements Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt in their correct order in the periodic table.

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[293] H is not so listed in the published version of table 25 (M18), i.e. in table 33 (P10). The latter table has H in group I.

[294] See n.260 of the present chapter.

[295] Op.cit., p.73-4; PLBA, 28.

CHAPTER IV

COLLECTION OF THE VARIOUS PERIODIC SYSTEMS COMPILED BY MENDELEEV (1869-1906)

The following collection of Mendeleev's periodic tables is arranged in a single numbered series in chronological order. Three kinds of table are distinguished: manuscript tables; published tables; and what may be called "lecture" tables, comprising tables presented by Mendeleev in lectures, and in one case, table 40, a table prepared in accordance with instructions given by Mendeleev which was placed on the wall of the large auditorium of the chemistry laboratory building of St. Petersburg University in 1876.[1] The dates taken for manuscript tables are dates of compilation[2]; for published tables, dates of publication; and for lecture tables, dates of presentation. Each table is designated according to its overall chronological ordinal number, and also (in parentheses) according to its type (by the letter M, P or L, denoting "manuscript", "published" or "lecture") and its chronological order as a particular type of table: thus, for example, table 38 (P14) is a published table which is the 38th table in the overall chronological series, and the 14th in the chronological series of published tables. Each of the manuscript tables is given in two versions: (a) a photographic reproduction of the original, and (b) a clarified, usually simplified, and where necessary translated reconstruction. Two versions - (a) and (b) - are also given for two of the lecture tables, tables 21 (L1) and 28 (L3); in the case of L3 the reconstructed version is a reproduction of a modern published printed representation.[3]

It will be noticed that in most of the tables - certainly of those up to table 58 (1902) - Mendeleev includes one or more question-marks. In his article on The periodic lawfulness of the chemical elements (G.) in Liebig's Annalen, 1871, he made the following remark, which although written

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[1] Where it is still to be found, in what is now the large auditorium of the Chemical Research Institute (Nauchno-issledovatel'skii khimicheskii institut) of Leningrad University.

[2] A few of these manuscripts were actually dated by Mendeleev. Most of them were not, however, and these have been dated by Kedrov on the basis of various kinds of evidence, e.g. the particular symbols used for certain elements; the atomic-weight values given; remarks made by Mendeleev on the same sheet of paper as that on which a particular table was drawn up; relationships to other, dated, manuscripts, etc.

[3] PLSM, 219.

specifically in connection with table 35 (P11) nevertheless serves as a general guide for the interpretation of question-marks in his periodic tables: "The mark ? placed in front of the symbol of an element signifies that because of insufficiency of research on that element[4] its place in the system is still not accurately known; and the mark ? placed after atomic-weight values indicates doubt concerning the atomic-weight value at present determined".[5] In addition to the two uses mentioned in this passage of 1871, a third purpose served by question-marks in some of Mendeleev's periodic tables is seen to be the indication of possible undiscovered elements - as, for example, in tables 5 (M5) and 8 (P1). In tables 51 (1889) and 53 (1889) - 56 (1898) we find what is undoubtedly a further function of the question-mark in its association with the entry "Di", viz. to query the status of didymium as a single element.

Although an attempt at completeness has been made in the present collection of Mendeleev's periodic tables, it is hardly likely that all manuscript tables ever drawn up by him will have been included (the manuscript tables given here all date from the period 1869-71). It is less unlikely that all lecture tables are included; and as regards published tables, it is probable that all such tables are in fact presented here.[6]

Below is a list of the various tables included in the collection, with their dates and source references. All of the manuscript and lecture tables

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[4] As may be seen from table 35 (P11), this refers to insufficiency of research on the chemical and physical properties of the element, particularly as regards the determination of valency.

[5] Op.cit., p.150; PLBA, 115.

[6] In general only full tables have been included, although a few early partial manuscript tables are also given. Of the published tables, where two or more identical tables appeared in different sources only one is given, listed according to the date of first appearance. Not included here, on the grounds that they are not so much periodic tables as lists of elements, are those arrangements of the elements, published in the 5th (1889) to 8th (1906) editions of Pr.Ch., where Mendeleev lists all of the elements in a single column in the order of their atomic weights (increasing from the top of the column downwards), and expresses the periodicity of properties by marking off alongside the elements the values of their valencies (with respect to H on one side of the column, and with respect to O on the other side) at distances from the elements reflecting the magnitude of these values. (An example of such an arrangement is presented in Ch.V, Fig. V - 2). Also not included, for the same reason, are other single-column or single-line lists of elements where the series or periods are marked off in some other way along the sequence, e.g. by bracketing together the elements of a given series, as in the list of elements given by Mendeleev in Bibl. 11, vol. 23, half-vol. 45, 1898, p.316 (PLBA, 250-3).

(the originals of which are to be found at Leningrad University[7]) have previously been reproduced in Soviet publications[8], and it is to these publications that reference is given. For those of Mendeleev's published tables which have likewise been reproduced in Soviet publications (and nearly all of them have been so reproduced) reference is given both to the original sources and to the Soviet sources.

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[7]Except for table 40 (see p. 196), all are to be found in the Mendeleev archive.

[8]Mainly by Kedrov, especially in Sc.Ar. In Sc.Ar. Kedrov has given also his own clarified and simplified reconstructions of Mendeleev's manuscript tables. The clarified and simplified reconstructions given in the present collection are not merely copies of those given by Kedrov; they have in many cases been further simplified compared with Kedrov's reconstructions, and where necessary translated.

List of tables.

Table 21 (L1), late autumn 1870 (probably early Nov., O.S.): Sc.Ar., 236; PLSM, 211.

Table 22 (M15), late autumn 1870 (probably early Nov., O.S.): Sc.Ar., 137.

Table 23 (M16), late autumn 1870 (probably early Nov., O.S.): Sc.Ar., 138; PLSM, 221.

Table 24 (M17), 17th Nov. (O.S.), 1870: Sc.Ar., 158; PLBA, phot. 12, p.68.

Table 25 (M18), 24th Nov. (O.S.), 1870: Sc.Ar., 166.

Table 26 (M19), 29th Nov. (O.S.), 1870: Sc.Ar., 184.

Table 27 (L2), late 1870-early 1871: this table is to be found in the notes made by M. Volkov at Mendeleev's lectures on inorganic chemistry, 1870-1, and is reproduced in printed form (with the correction of two obvious errors in Volkov's manuscript) in Bibl. 75, p.75. The date of compilation of this table by Mendeleev appears, from a comparison with his other tables, to have been 1869. The version of the table given in the present collection is reproduced from Bibl. 75.

Table 28 (L3), early 1871: version (a), a photocopy of the original, is given in Sc.Ar., 275, and in PLSM, 218; version (b), a printed reconstruction, is given in PLSM, 219.

Table 29 (M20), February (?), 1871: Sc.Ar., 220.

Table 30 (P7), February 1871: from the article A natural system of the elements (R.), p.31 (PLBA, 76).

Table 31 (P8), late February, 1871: the larger and more detailed of two tables given on a folding sheet (headed D. Mendeleev's natural system of the elements, R.) found near the beginning of Pr.Ch., R-1, part II (PLBA, folding sheet between pp. 340 and 341 - the larger and more detailed of the two tables facing p.340).

Table 32 (P9), late February, 1871: the table accompanying table 31 (P8) on the sheet D. Mendeleev's natural system of the elements (R.).

Table 33 (P10), 18th March (O.S.), 1871: On the place of cerium (G.), pp. 50-1 (PLBA, 66-7). The table given in the present collection is the Russian version from PLBA.

Table 34 (M21), early summer, 1871: Sc.Ar., 528; PLBA, phot. 13, p.179.

Table 35 (P11), 6th November 1871: Tabelle I from The periodic lawfulness of the chemical elements (G.), Liebig's Annalen, p.149 (PLBA, 114).

Table 36 (P12) 6th November 1871: Tabelle II, The periodic lawfulness of the chemical elements (G.), Liebig's Annalen, p.151 (PLBA, 116).

Table 37 (P13), August 1872: table headed An attempt at a system of the elements, based upon atomic weight and chemical resemblance (R.), Pr.Ch., R-2, part I (1872) p.iv (PLBA, 341).

Table 38 (P14), 1873: on a folding sheet at the front of Pr.Ch., R-2, part II (1873) (PLBA, folding sheet between pp.340 and 341; facing p.341).

Table 39 (P15), 1875: A note in connection with the discovery of gallium (F.), Comptes rendus, 81 (1875) 969-72; p.969 (PLBA, 199). The Russian version from PLBA is given in the present collection.

Table 40 (L4), 1876: see earlier in the present chapter, p.196. A photographic reproduction is given in Bibl.75, p.144. A typescript copy is given in the present collection.

Table 41 (P16), June 1877: table headed The periodic system of the chemical elements, based upon atomic weight and chemical resemblance (R.), Pr.Ch., R-3 (1877) part I, p.xii (PLBA, 342).

Table 42 (P17), June 1877: Pr.Ch., R-3 (1877) part II, p.848 (PLBA, 343).

Table 43 (P18), June 1877: table headed Periodic system of the elements (R.), Pr.Ch., R-3 (1877) part II, p.1432 (PLBA, 346).

Table 44 (P19), July 1879: Moniteur Scientifique [3], 9 (1879) 691-3; p.692 (PLBA, 395). The Russian version from PLBA, rather than the original French version, is given in the present collection.

Table 45 (P20), 1880: On the history of the periodic law (G.), Berichte, 13 (1880) 1796-1804; p.1804 (PLBA, 406).

Table 46 (P21), September 1881: table headed Periodic system of the chemical elements - Arrangement of the elements by groups and series (R.), Pr.Ch., R-4, part I (1881) p.xi (PLBA, 347).

Table 47 (P22), September 1881: table headed Periodic system of the chemical elements, based upon atomic weight, expressing their resemblances and corresponding to their capacity for combination with oxygen, hydrogen and other elements - Arrangement of the elements by periods (R.), Pr.Ch., R-4, part I (1881) p.xvi; an identical table is given in Pr.Ch., part II (1882) 1158 (PLBA, 348).

Table 48 (P23), January 1882: Pr.Ch., R-4, part II (1882) 679 (PLBA, 349).

Table 49 (L5), late 1886: presented in Mendeleev's Lectures on theoretical chemistry, delivered in higher courses for women (R.), 1886-7, lecture 4 (PLSM, 257; Colls., 15, 468).

Table 50 (L6), late 1886: presented in Lectures on theoretical chemistry, delivered in higher courses for women (R.), 1886-7, lecture 5 (PLSM, 270; Colls., 15, 482).

Table 51 (P24), May 1889: table headed Arrangement of the elements by groups and series (R.), Pr.Ch., R-5 (1889) p.vii (PLBA, 352).

Table 52 (P25), May 1889: table headed Distribution of the elements by periods (R.), Pr.Ch., R-5 (1889) p.xviii (PLBA, 353).

Table 53 (P26), May 1889: Pr.Ch., R-5 (1889) 461 (PLBA, 354).

Table 54 (P27), February 1895: table headed Arrangement of the elements by groups and series (R.), Pr.Ch., R-6 (1895) p.x (PLBA, 355).

Table 55 (P28), February 1895: table headed Periodic system and atomic weights of the elements (R.), Pr.Ch., R-6 (1895) p.xi (PLBA, 356-7).

Table 56 (P29), 1898: Bibl.11, vol. 23, half-vol. 45, 1898, p.317 (PLBA, 255).

Table 57 (P30), November 1902: table headed Periods of the chemical elements, taking the atomic weight of oxygen = 16 (R.), Pr.Ch., R-7 (1902-3) p.ix (PLBA, 362-3).

Table 58 (P31), 1902: table headed Periodic system of the elements by groups and series (R.), Pr.Ch., R-7 (1902-3) p.x (PLBA, 364).

Table 59 (P32), 1902: Pr.Ch., R-7 (1902-3) 460 (PLBA, 365).

Table 60 (P33), 1903: Attempt at a chemical conception of the world-ether (R.) (see n.80 to Ch.I of this thesis for full reference). The version of this table given in the present collection is reproduced from Pr.Ch., E-3 (1905; from R-7), vol. II, appendix III, p.519.

Table 61 (P34), 1904: Bibl.11, vol. 40, half-vol. 80, 1904, p.635 (PLBA, 422-3).

Table 62 (P35), 1905: 2nd edn. of Attempt at a chemical conception of the world-ether (R.), p.25 (PLBA, 497).

Table 63 (P36), 1906: table headed Periods of the chemical elements and the weights of their atoms, taking the atomic weight of oxygen = 16 (R.), Pr.Ch., R-8 (1906) p.VII (PLBA, 366-7).

Table 64 (P37), 1906: table headed Periodic system of the elements by groups and series (R.), Pr.Ch., R-8, (1906) p.viii (PLBA, 368).

Table 65 (P38), 1906: Pr.Ch., R-8 (1906) 255 (PLBA, 369).

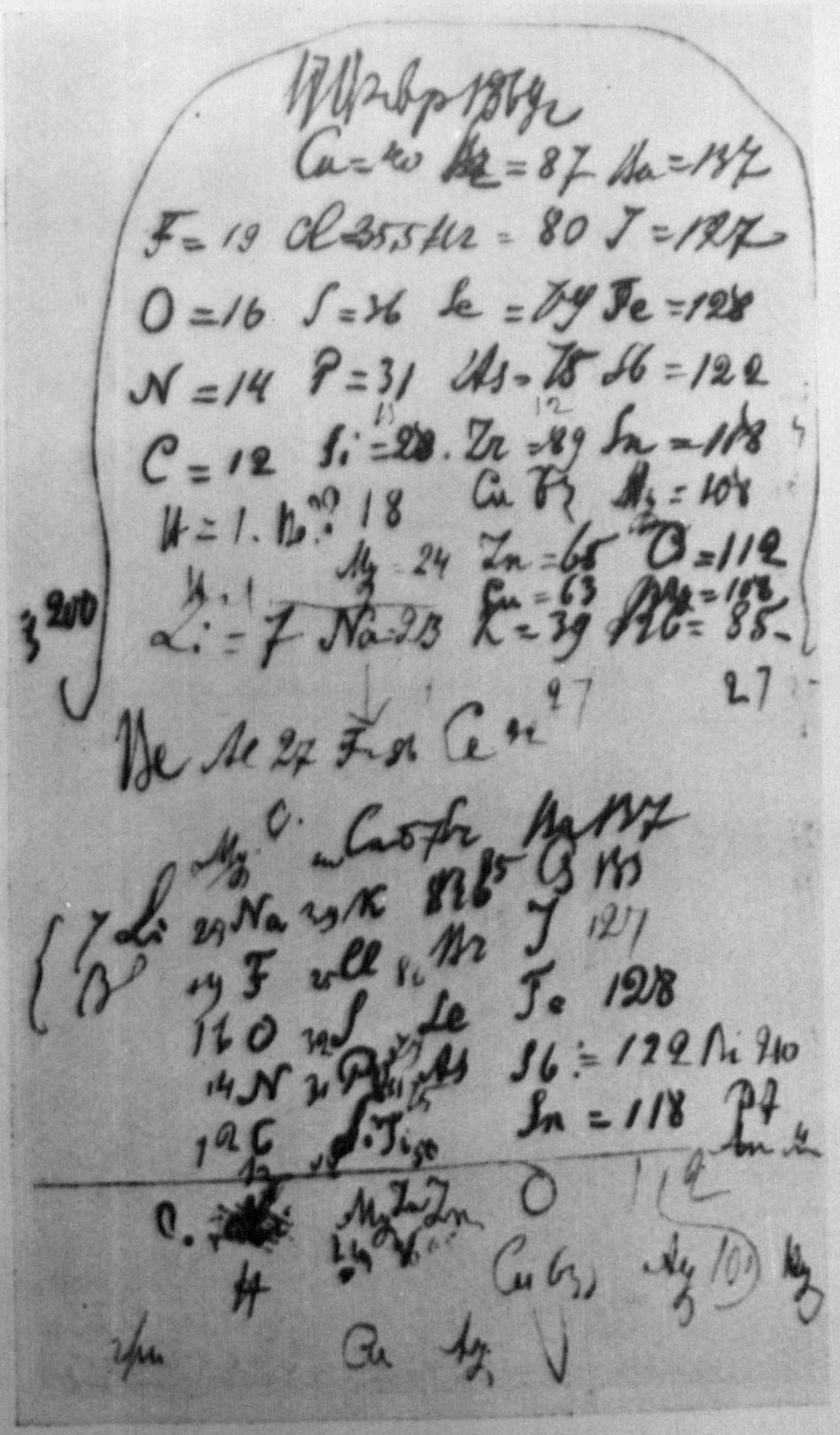


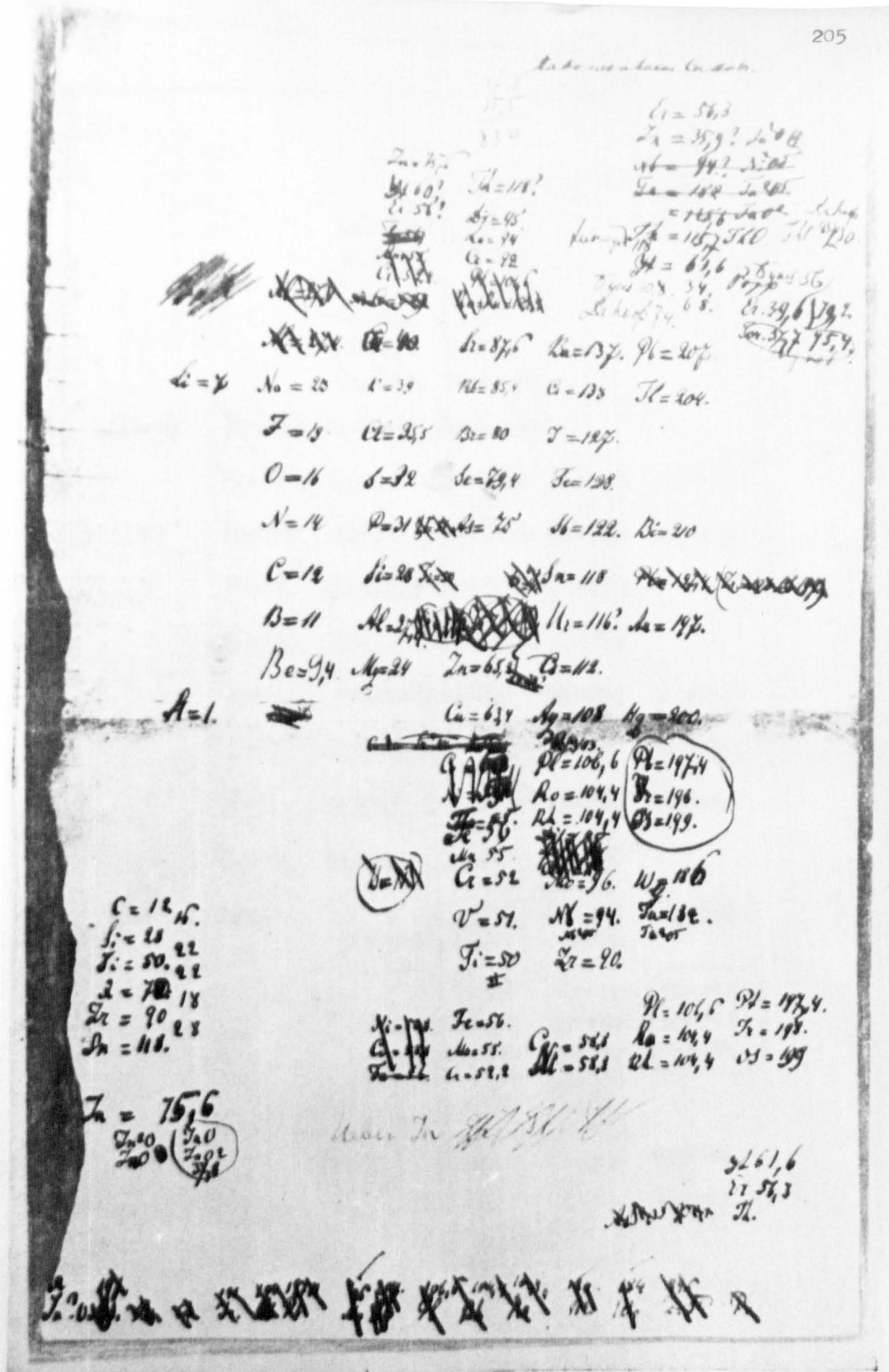
Рис. 2.
Автограф двух неполных таблиц элементов
(17 февраля 1869 г.)

17 Feb 1869

	Ca = 40	Sr = 87	Ba = 137
F = 19	Cl = 35·5	Br = 80	J = 127
O = 16	S = 36	Se = 79	Te = 128
N = 14	P = 31	As = 75	Sb = 122
C = 12	Si = 28	Zr = 89	Sn = 118
H = 1 Be??	18	Cu 63	Ag = 108
	Mg = 24	Zn = 65	Cd = 112
H = 1		Cu = 63	Ag = 108
Li = 7	Na = 23	K = 39	Rb = 85
Be	Al 27	Fe 56	Ce 92

	Mg	$_{40}$Ca	$_{87}$Sr	Ba 137	
$_{7}$Li	$_{23}$Na	$_{39}$K	Rb^{85}	Cs 133	
Be	$_{19}$F	$_{35}$Cl	$_{80}$Br	J 127	
	$_{16}$O	$_{32}$S	$_{79}$Se	Te 128	
	$_{14}$N	$_{31}$P V$_{51}$	$_{75}$As	Sb = 122	Bi 210
	$_{12}$C	Si Ti$_{50}$		Sn = 118	Pt
	B				Au
	~~7Li~~	Mg In	Zn		
	H	24 36	65	Cu 63 Ag 108	Hg
		Cu	Ag		

Table 1 (M1) (b).



Фотокопия 1. Автограф раннего варианта периодической системы элементов.

We need the sp. ht. of Ca, Ba, Sr.

Er=56·3
In=35·9? In^2O
~~Nb=94? Nb^2O^5~~
~~Ta=182 Ta^2O^5~~
=144·6 TaO^2 Delafontaine?
Th=115·7 ThO ThO^2 230
Yt=61·6
Bunsen 56
Er 396 | 792
Ter 37·7 75·4 non-exist. acc. to Bunsen

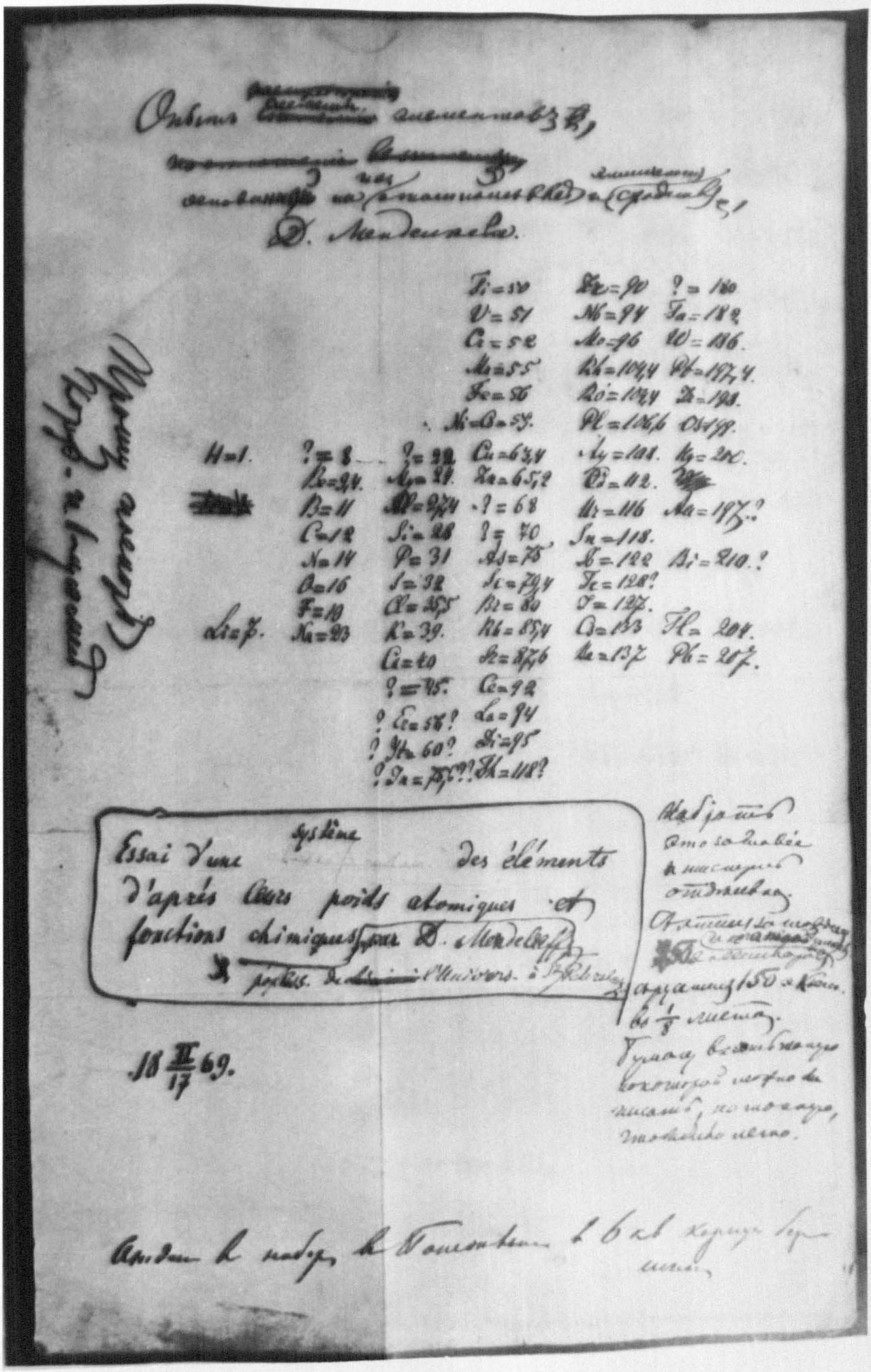
In=75·6
Yt 60?
Er=56?
~~Fe=56~~
Mn=55
Cr=52·2
Th=118?
Di=95
La=94
Ce=92
Pl=106·6

~~Be=14~~ ~~Al=27·4~~ ~~Ni=Co=59~~ ~~Ro=Ru=104·4~~

	~~Al=27·4~~	Ca=40	Sr=87·6	Ba=137	Pb=207
Li=7	Na=23	K=39	Rb=85·4	Cs=133	Tl=204
	F=19	Cl=35·5	Br=80	J=127	
	O=16	S=32	Se=79·4	Te=128	
	N=14	P=31 ~~V=51~~	As=75	Sb=122	Bi=210
	C=12	Si=28 ~~Ti=50~~	~~Zr=90~~ 44·8	Sn=118	~~Pt=197·4~~ ~~(Ir=198, Os=199)~~
	B=11	~~Al=27·4~~ ~~Cr=52·2~~	~~In=75·6?~~	Ur=116?	Au=197
	Be=9·4	Mg=24	Zn=65·2	Cd=112	
H=1	~~H=1~~		Cu=63·4	Ag=108	Hg=200
		~~Ca? 20 Sr? 44 Ba? 68~~		~~Pb? 103~~	
			~~Co=60~~	Pl=106·6	Pt=197·4
			~~Ni=59~~	Ro=104·4	Ir=198
			Fe=56	Rh=104·4	Os=199
			Mn=55	~~Di=95~~ ~~La=94~~ ~~Ce=92~~	
		~~Bo=11?~~	Cr=52	Mo=96	W=186
			V=51	Nb=94 Nb^2O^5	Ta=182 Ta^2O^5
			Ti=50	Zr=90	

C=12 (16)
Si=28 (22)
Ti=50 (22)
X=72 (18)
Zr=90 (28)
Sn=118

Table 2 (M2) (b).



D. Mendeleeff.

Ti=50 Zr=90 ?=180
V=51 Nb=94 Ta=182
Cr=52 Mo=96 W=186.
Mn=55 Rh=104,4 Pt=197,4.
Fe=56 Ru=104,4 Ir=198.
Ni=Co=59. Pl=106,6 Os=199.
H=1. ?=8 ?=22 Cu=63,4 Ag=108. Hg=200.
Be=9,4. Mg=24. Zn=65,2 Cd=112.
B=11 Al=27,4 ?=68 Ur=116 Au=197.?
C=12 Si=28 ?=70 Sn=118.
N=14 P=31 As=75 Sb=122 Bi=210.?
O=16 S=32 Se=79,4 Te=128?
F=19 Cl=35,5 Br=80 J=127.
Li=7. Na=23 K=39. Rb=85,4 Cs=133 Tl=204.
Ca=40 Sr=87,6 Ba=137 Pb=207.
?=45. Ce=92
? Er=56? La=94
? Yt=60? Di=95
? In=75,6?! Th=118?

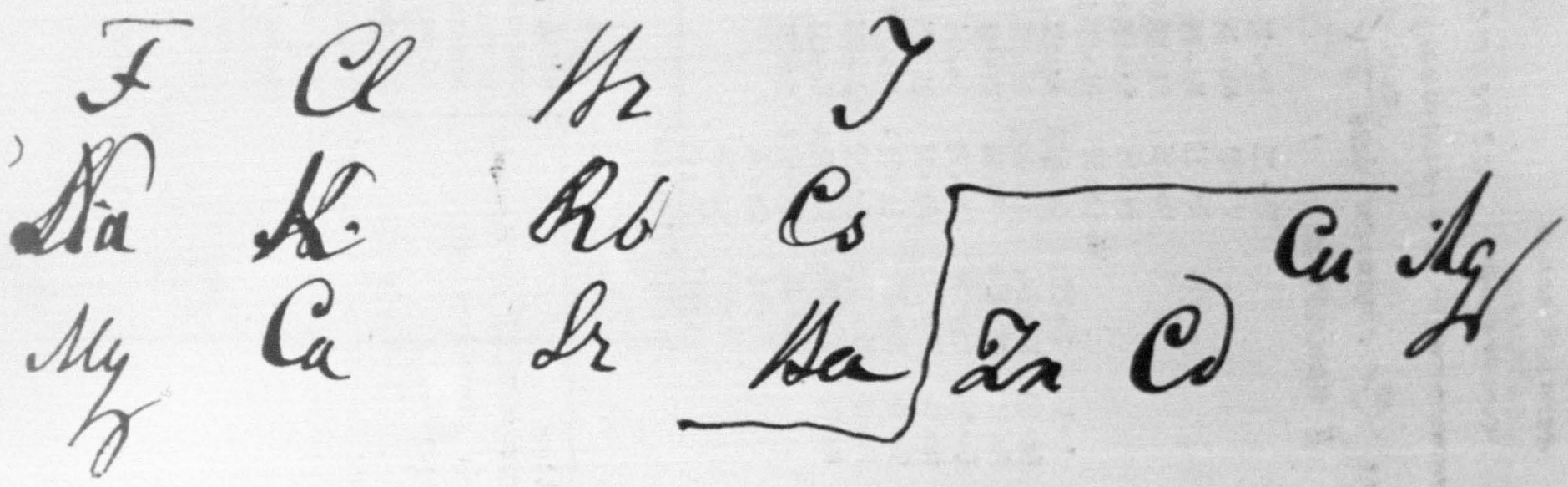
Essai d'une système des éléments d'après leurs poids atomiques et fonctions chimiques par D. Mendeleeff professeur de chimie à l'Université de St-Pétersbourg

18 II/17 69.

Table 3 (M3)(a)

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104·4	Pt = 197·4
			Fe = 56	Ro = 104·4	Ir = 198
			Ni = Co = 59	Pl = 106·6	Os = 199
H = 1	? = 8	? = 22	Cu = 63·4	Ag = 108	Hg = 200
	Be = 9·4	Mg = 24	Zn = 65·2	Cd = 112	~~? ∈~~
~~H ∈ I~~	B = 11	Al = 27·4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79·4	Te = 128?	
	F = 19	Cl = 35·5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85·4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87·6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56?	La = 94		
		?Yt = 60?	Di = 95		
$18\frac{II}{17}69$		?In = 75·6?	?Th = 118?		

Table 3 (M3) (b)



Фотокопия 1. **Часть таблицы элементов с указанием на сдваивание рядов (ув.)**

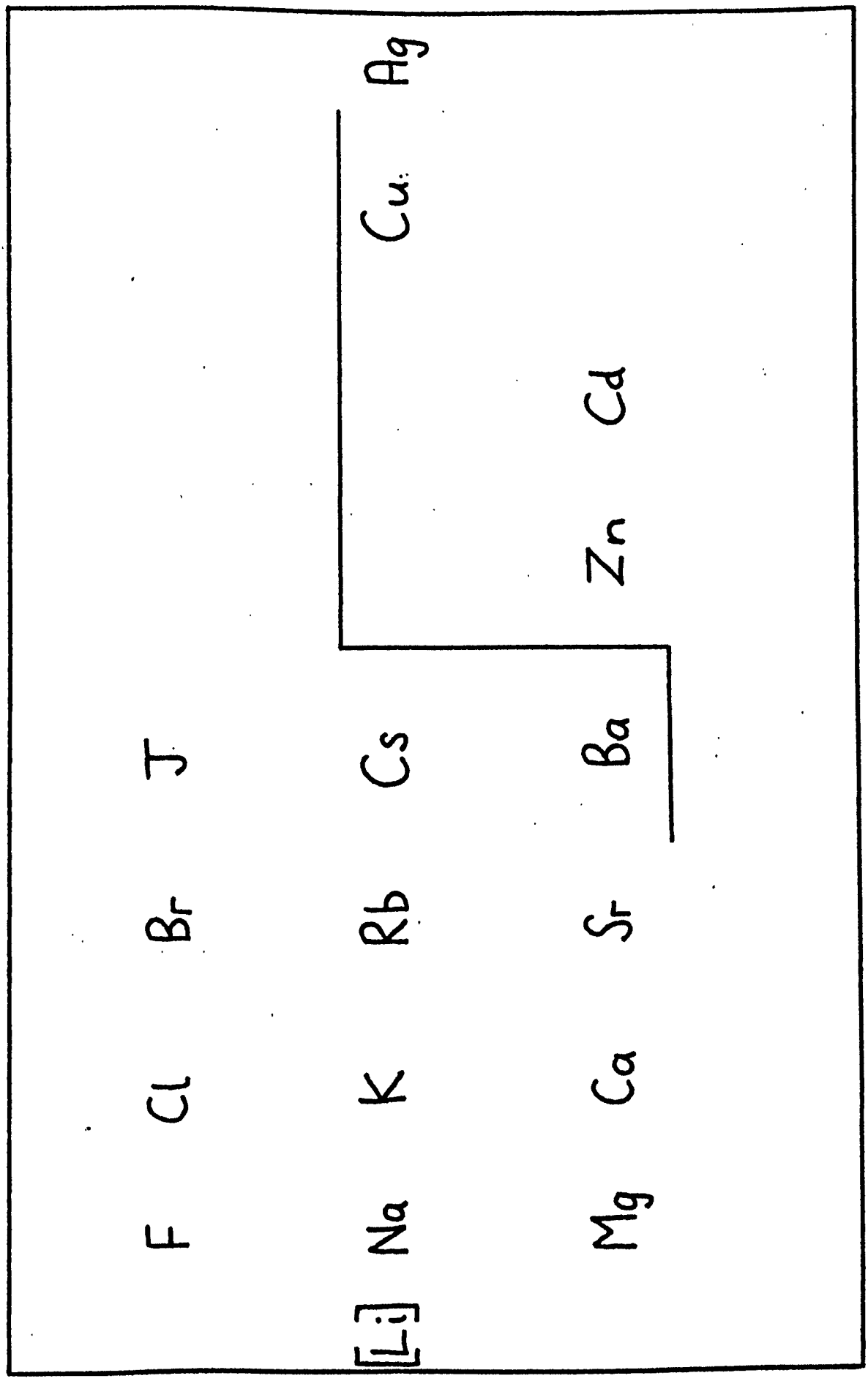
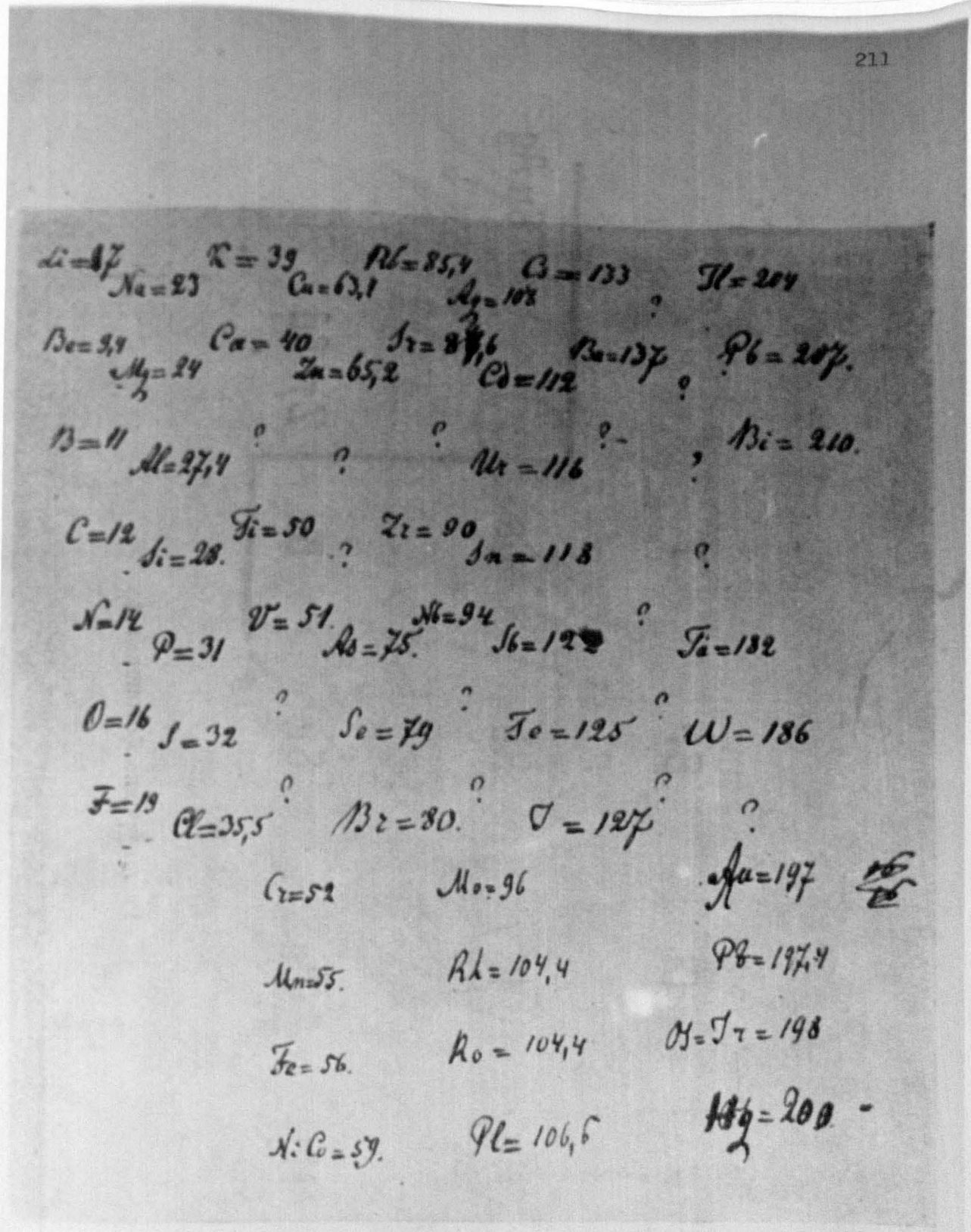


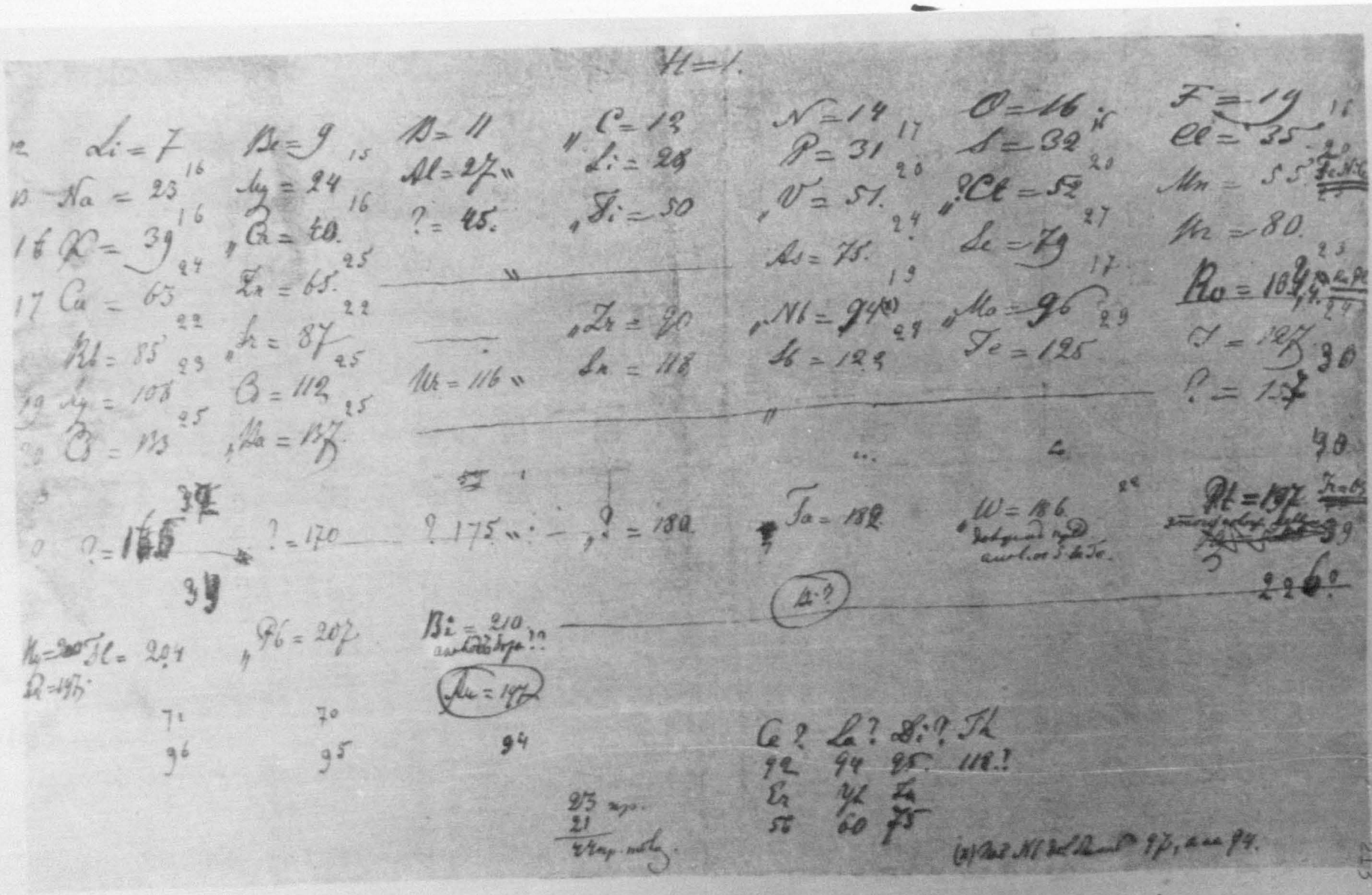
Table 4 (M4)(b).



Фотокопия 2. Автограф таблицы элементов с частично укороченными рядами (ум.)

Li=7	K=39	Rb=85·4	Cs=133	Tl=204
Na=23	Cu=63·4	Ag=108	?	
Be=9·4	Ca=40	Sr=87·6	Ba=137	Pb=207
Mg=24	Zn=65·2	Cd=112	?	
B=11	?	?	?	Bi=210
Al=27·4	?	Ur=116	?	
C=12	Ti=50	Zr=90		
Si=28	?	Sn=118	?	
N=14	V=51	Nb=94	?	
P=31	As=75	Sb=122	Ta=182	
O=16	?	?	?	
S=32	Se=79	Te=125	W=186	
F=19	?	?	?	
Cl=35·5	Br=80	J=127	?	
	Cr=52	Mo=96	Au=197	
	Mn=55	Rh=104·4	Pt=197·4	
	Fe=56	Ro=104·4	Os=Ir=198	
	NiCo=59	Pl=106·6	Hg=200	

Table 5 (M5) (b).



Фотокопия 3. **Автограф раннего варианта короткой таблицы элементов (ум.)**

Table 6 (M6)(a)

Table 6 (M6) (b).

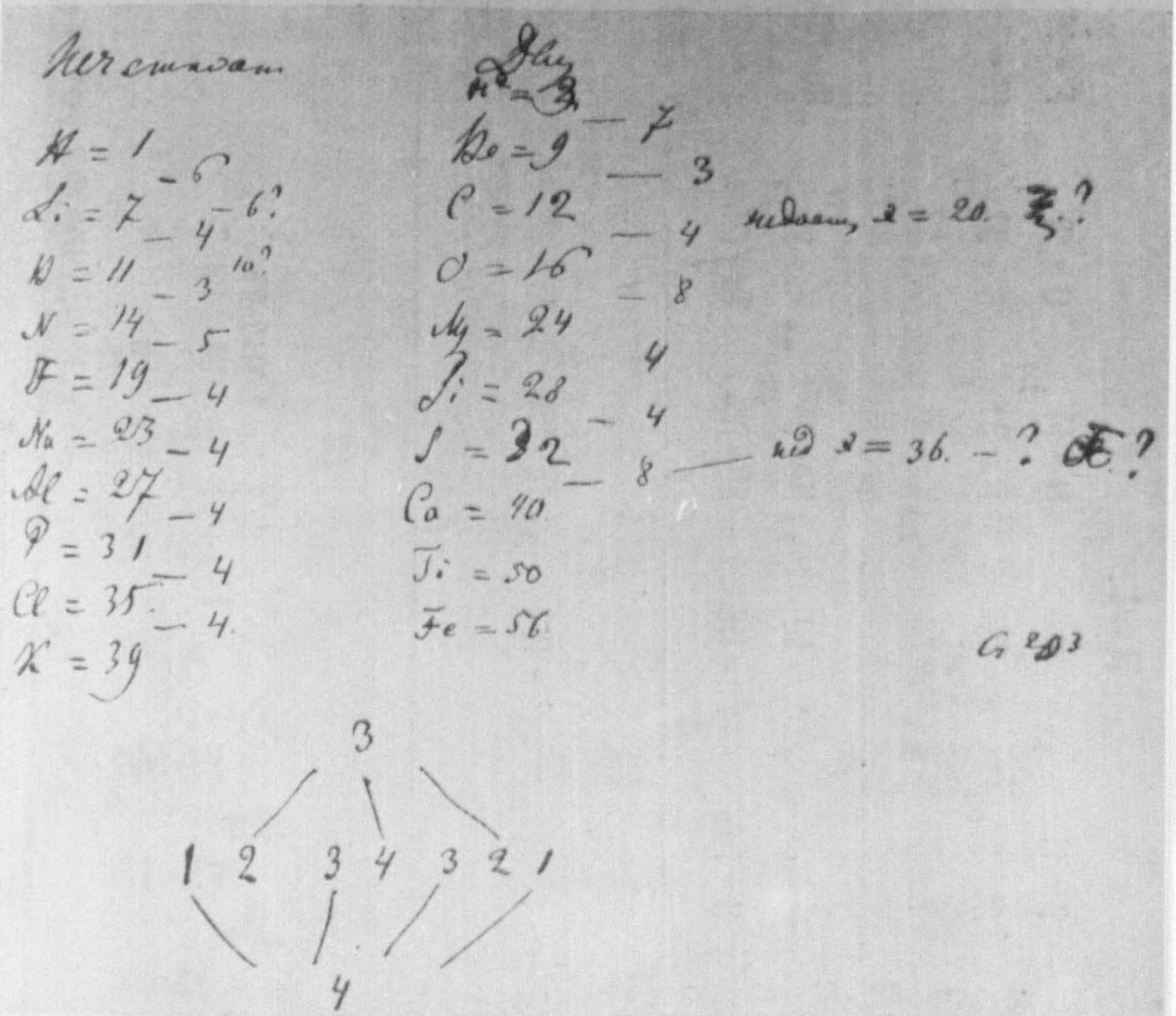
H=1

Li=7	Be=9	B=11	"C=12	N=14	O=16	F=19	
Na=23	Mg=24	Al=27"	Si=28	P=31	S=32	Cl=35	
K=39	"Ca=40	?=45	"Ti=50	"V=51	"?Cr=52	Mn=55	Fe Ni Co
Cu=63	Zn=65	—— " ——		As=75	Se=79	Br=80	
Rb=85	"Sr=87	——	"Zr=90	"Nb=94(x)	"Mo=96	Ro=104·4	~~Ro~~ Ru Pl
Ag=108	Cd=112	U=116"	Sn=118	Sb=122	Te=125	J=127	
Cs=133	"Ba=137	——	" ——			?=157	
?=165	?=170	?=175"	"?=180	Ta=182	"W=186 must represent an analogue of S,Se,Te.	Pt=197 the position of this is wrong Hg=200	Ir=Os
Hg=200				Bi?			
Tl=204	"Pb=207	Bi=210 analogue of boron??		——		226?	
Au=197		Au 197					

Ce? La? Di? Th
92 94 95 118?

Er Yt In
56 60 75

(x) At.wt. of Nb must be 97, and not 94.



Фотокопия 4. Вычисление разности атомных весов у элементов различной атомности (ум.)

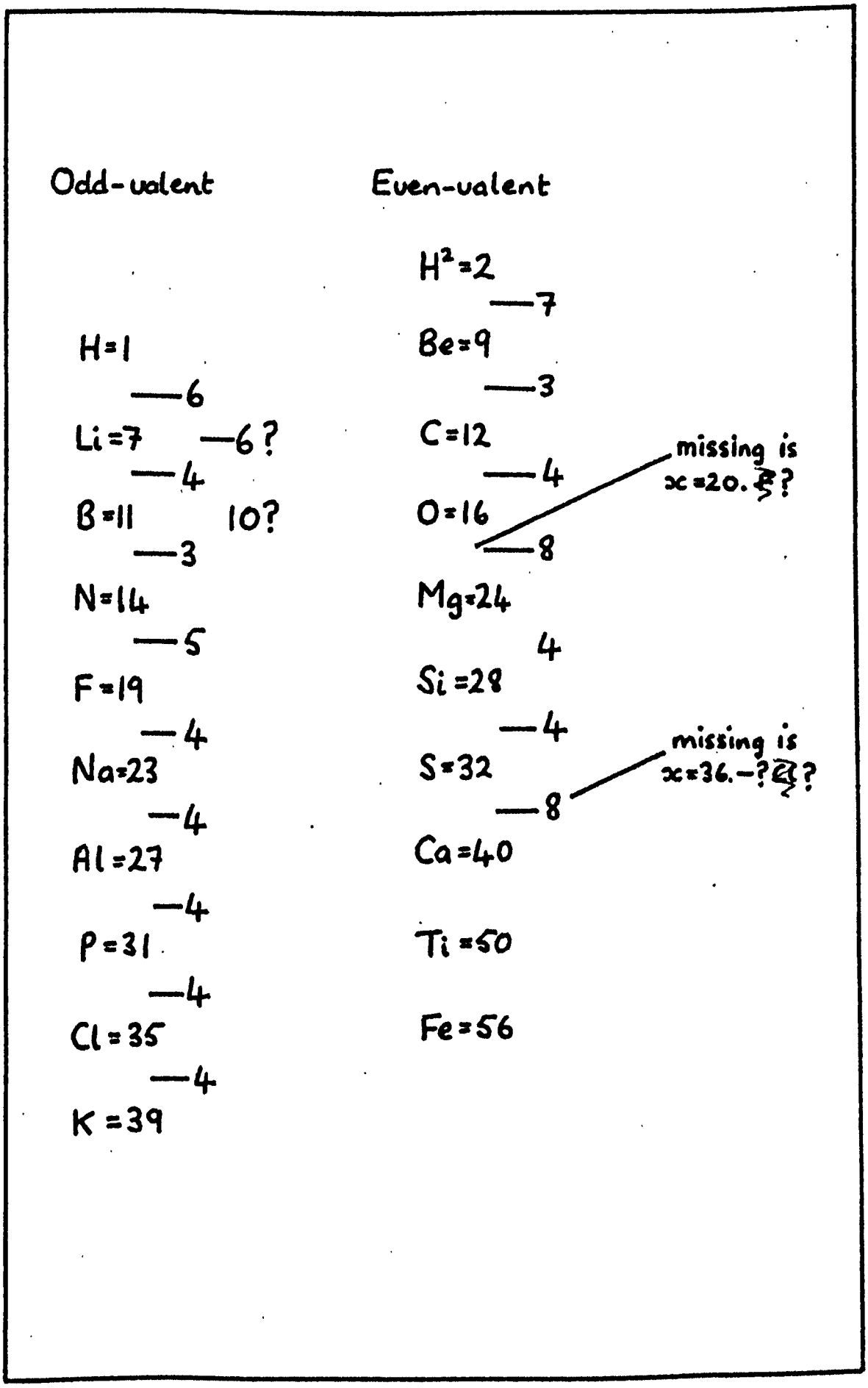

Odd-valent
Even-valent
H=1
—6
Li=7
—6?
—4
B=11
10?
—3
N=14
—5
F=19
—4
Na=23
—4
Al=27
—4
P=31
—4
Cl=35
—4
K=39
H²=2
—7
Be=9
—3
C=12
—4
O=16
—8
Mg=24
4
Si=28
—4
S=32
—8
Ca=40
Ti=50
Fe=56
missing is x=20.-?
missing is x=36.-?

Table 7 (M7) (b).

ОПЫТ СИСТЕМЫ ЭЛЕМЕНТОВ, ОСНОВАННОЙ НА ИХ АТОМНОМ ВЕСЕ И ХИМИЧЕСКОМ СХОДСТВЕ

			Ti = 50	Zr = 90	? = 180.
			V = 51	Nb = 94	Ta = 182.
			Cr = 52	Mo = 96	W = 186.
			Mn = 55	Rh = 104,4	Pt = 197,4
			Fe = 56	Ru = 104,4	Ir = 198.
			Ni = Co = 59	Pl = 106,6	Os = 199.
H = 1			Cu = 63,4	Ag = 108	Hg = 200.
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28.	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204.
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.
		? = 45	Ce = 92		
		? Er = 56	La = 94		
		? Yt = 60	Di = 95		
		? In = 75,6	Th = 118?		

Д. Менделеев.

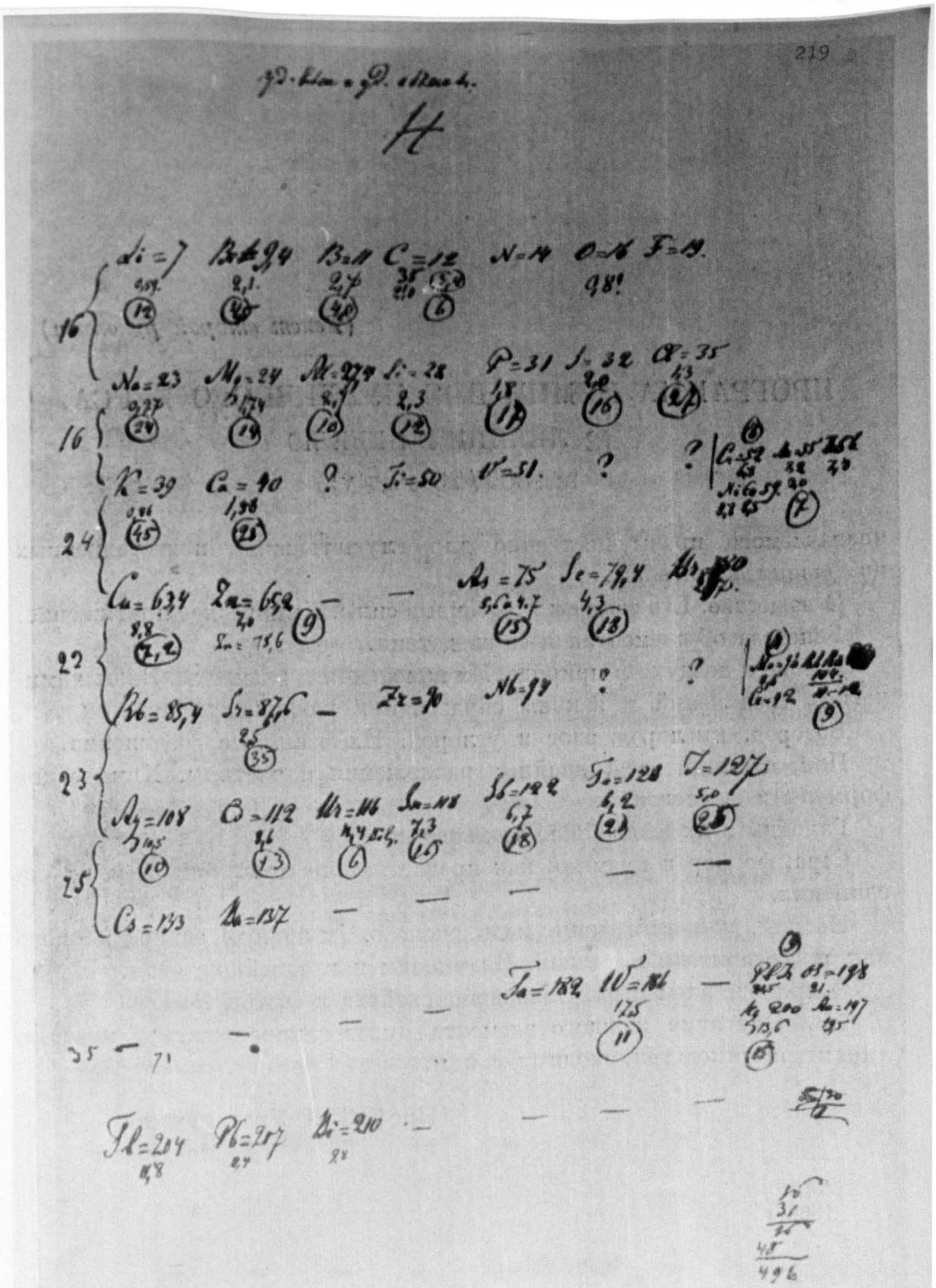
Table8 (P1)

			Ti = 50	Zr = 90	? = 180	
			V = 51	Nb = 94	Ta = 182	
			Cr = 52	Mo = 96	W = 186	
			Mn = 55	Rh = 104,4	Pt = 197,4	
			Fe = 56	Ru = 104,4	Ir = 198	
			Ni = Co = 59	Pl = 106,6	Os = 199	
H = 1			Cu = 63,4	Ag = 108	Hg = 200	
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112		
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?	
	C = 12	Si = 28	? = 70	Sn = 118		
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210	
	O = 16	S = 32	Se = 79,4	Te = 128?		
	F = 19	Cl = 35,5	Br = 80	J = 127		
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204	
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.	
		? = 45	Ce = 92			
		? Er = 56	La = 94			
		? Yt = 60	Di = 95			
		? In = 75,6	Th = 118?			

Table9 (P2)

Li	Na	K	Cu	Rb	Ag	Cs	—	Tl
7	23	39	63,4	85,4	108	133		204
Be	Mg	Ca	Zn	Sr	Cd	Ba	—	Pb
B	Al	—	—	—	Ur	—	—	Bi?
C	Si	Ti	—	Zr	Sn	—	—	—
N	P	V	As	Nb	Sb	—	Ta	—
O	S	—	Se	—	Te	—	W	—
F	Cl	—	Br	—	J	—	—	—
19	35,5	58	80	190	127	160	190	220.

Table10 (P3)



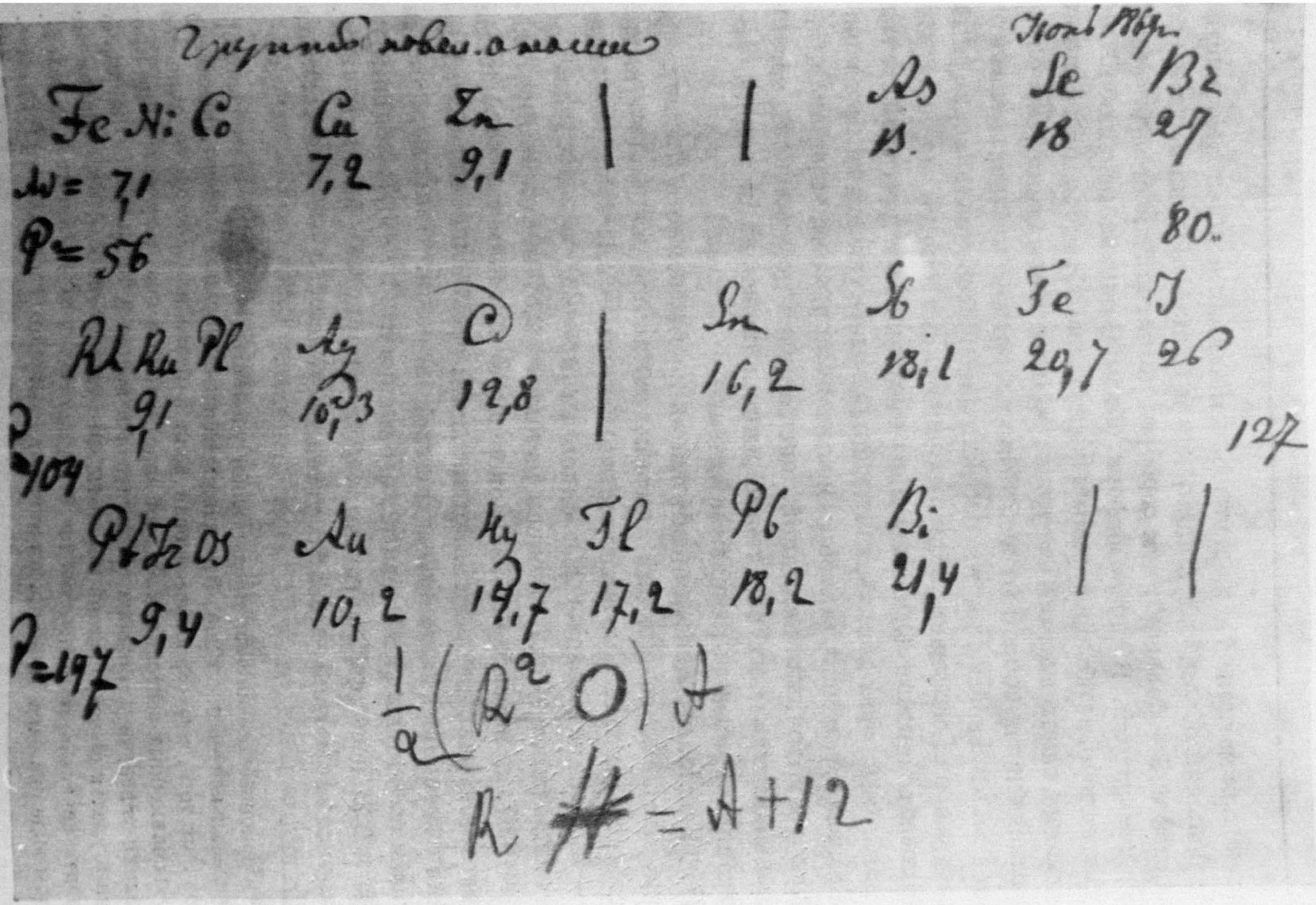
Фотокопия 5. Автограф короткой таблицы элементов с атомными объемами: «Удельные веса и удельные объемы» (ум.)

Table 11 (M8)(a)

H

	Li=7	Be=9·4	B=11	C=12	N=14	O=16	F=19	
16								
	Na=23	Mg=24	Al=27·4	Si=28	P=31	S=32	Cl=35	
16								
	K=39	Ca=40	?	Ti=50	V=51	?	?	Cr=52 Mn=55 Fe=56 Ni Co 59
24								
	Cu=63·4	Zn=65·2	—	—	As=75	Se=79·4	Br=80	
22		In=75·6						
	Rb=85·4	Sr=87·6	—	Zr=90	Nb=94	?	?	Mo=96 Rh Ru Pl Ce=92
23								
	Ag=108	Cd=112	Ur=116	Sn=118	Sb=122	Te=128	J=127	
25								
	Cs=133	Ba=137	—	—	—	—	—	
	—	—	—	—	Ta=182	W=186	—	Pt Ir Os=198 Hg=200 Au=197
	Tl=204	Pb=207	Bi=210	—	—	—	—	

Table 11 (MB) (b).



Фотокопия 8. Часть больших периодов элементов с атомными объемами: «Группы по величине атомов»

June 1869

Groups according to the magnitude of the atoms

	Fe Ni Co	Cu	Zn			As	Se	Br
Av =	7·1	7·2	9·1			13	18	27
P =	56							80
	Rh Ru Pl	Ag	Cd		Sn	Sb	Te	J
	9·1	10·3	12·8		16·2	18·1	20·7	26
P=104								127
	Pt Ir Os	Au	Hg	Tl	Pb	Bi		
	9·4	10·2	14·7	17·2	18·2	21·4		
P=197								

Table 12 (Mg) (b).

Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19
Na = 23	Mg = 24	Al = 28,4	Si = 28	P = 31	S = 32	Cl = 35,5
K = 39	Ca = 40	—	—	—	—	—
	Zn = 65	—	—	As = 75	Se = 79	Br = 80
Rb = 85	Sr = 87	—	?Zr = 90	—	—	—
Ag = 108	Cd = 112	—*	Sn = 118	Sb = 122	Te = 128	J = 127
Cs = 133	Ba = 137.					

Приведенная здесь система элементов удовлетворяет не только естественной их группировке, но только отличию их по химическому

* В первом сообщении я считал уран (Ur = 116) занимающим это место системы; но в настоящее время, по многим соображениям, считаю это неверным, как о том будет сообщено, когда начатые в этом отношении исследования будут окончены.

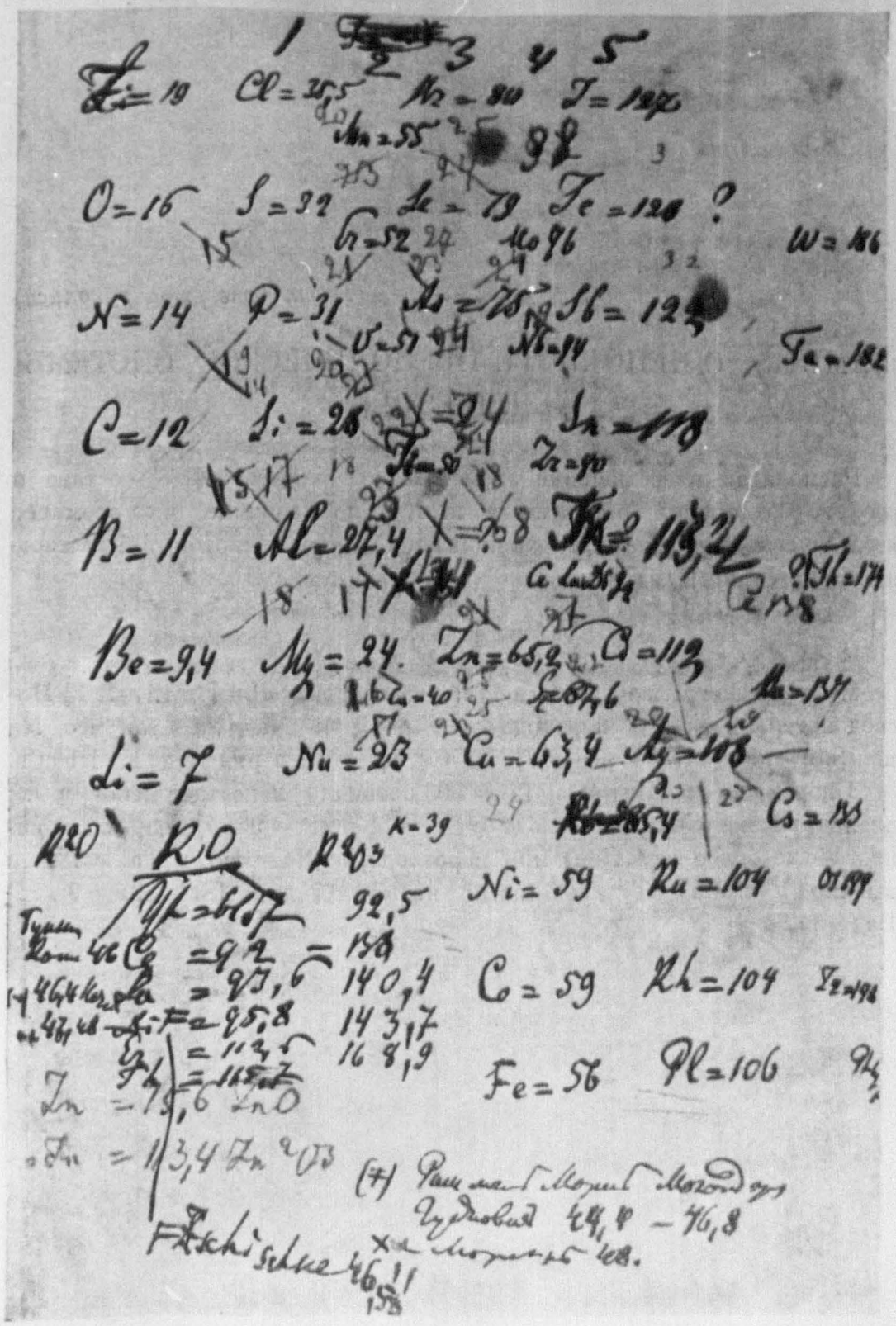
Table13 (P4)

Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19
Na = 23	Mg = 24	Al = 27,4	Si = 28	P = 31	S = 32	Cl = 35,5
K = 39	Ca = 40	—	—	—	—	—
Cu = 63,4	Zn = 65,2	—	—	As = 75	Se = 79,4	Br = 80
Rb = 85,4	Sr = 87,6	—	—	—	—	—
Ag = 108	Cd = 112	—	Sn = 118	Sb = 122	Te = 128?	J = 127
Cs = 133	Ba = 137	—	—	—	—	—

Table14 (P5)

Li	Be	B	C	N	O	F			
Na	Mg	Al	Si	P	S	Cl			
K	Ca	—	Ti	V	Cr	Mn	Fe	Co	Ni*
*Cu	Zn	—	—	As	Se	Br			
Rb	Sr	—	Zr	Nb	Mo	—	Rh	Ru	Pl*
*Ag	Cd	—	Sn	Sb	Te	J			
Cs	Ba	—	—	Ta	W	—	Pt	Ir	Os

Table15 (P6)

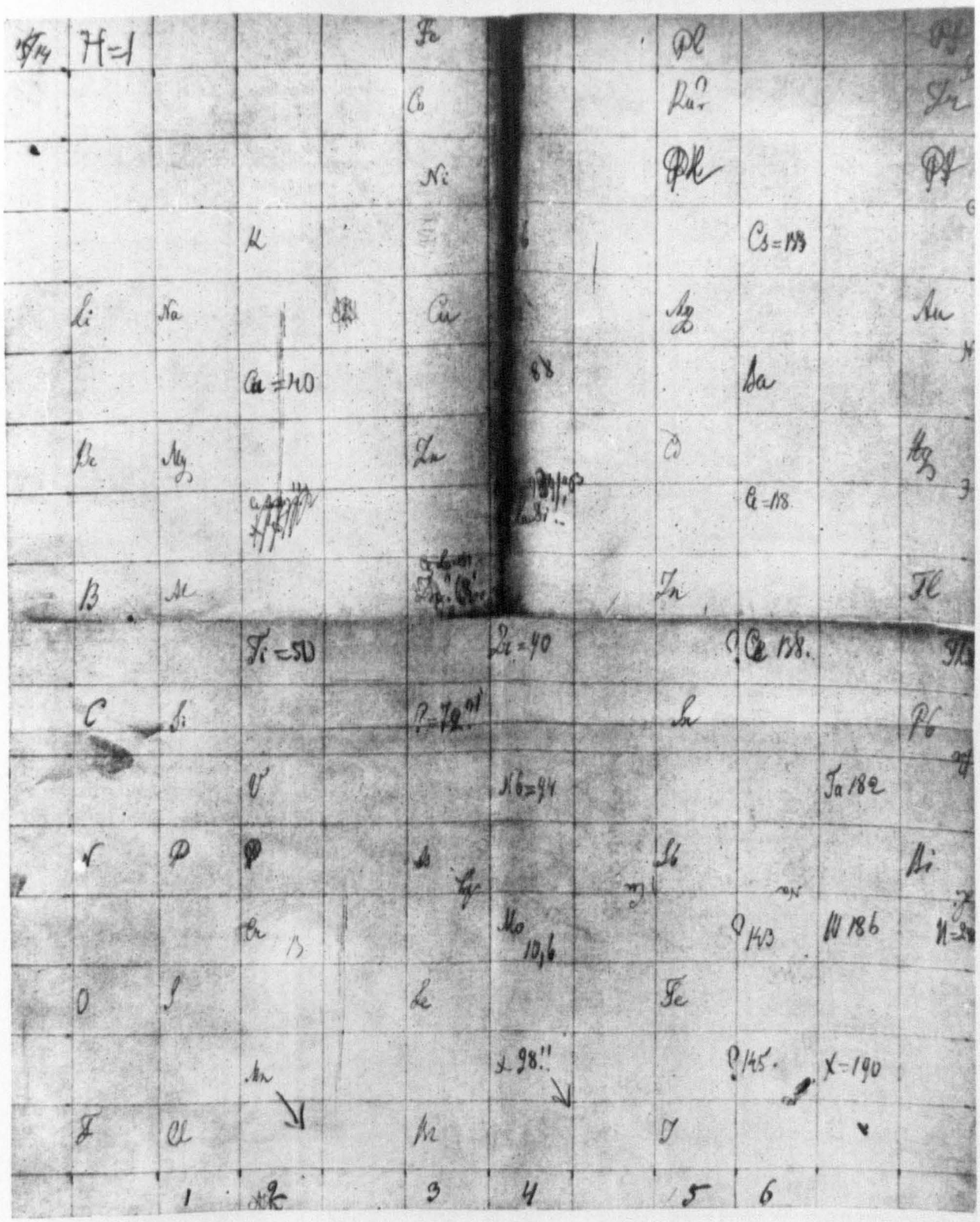


Фотокопия 12. Набросок короткой таблицы элементов с первыми исправлениями атомных весов

Table 16 (M10)(a)

1	~~Fe=56~~ 2	3	4	5
F=19	Cl=35·5	Br=80	J=127	
	Mn=55	98		
O=16	S=32	Se=79	Te=128?	
	Cr=52	Mo=96		W=186
N=14	P=31	As=75	Sb=122	
	V=51	Nb=94		Ta=182
C=12	Si=28	x=74	Sn=118	
	Ti=50	Zr=90		
B=11	Al=27·4	x=68	In=113·4	
	x=44	CeLaDi92	Ce138	?ITh=174
Be=9·4	Mg=24	Zn=65·2	Cd=112	
	Ca=40	Sr=87·6	Ba=137	
Li=7	Na=23	Cu=63·4	Ag=108	
	K=39	Rb=85·4	Cs=133	
		Ni=59	Ru=104	Os 199
		Co=59	Rh=104	Ir=198
		Fe=56	Pl=106	Pt197

Table 16 (M10) (b).

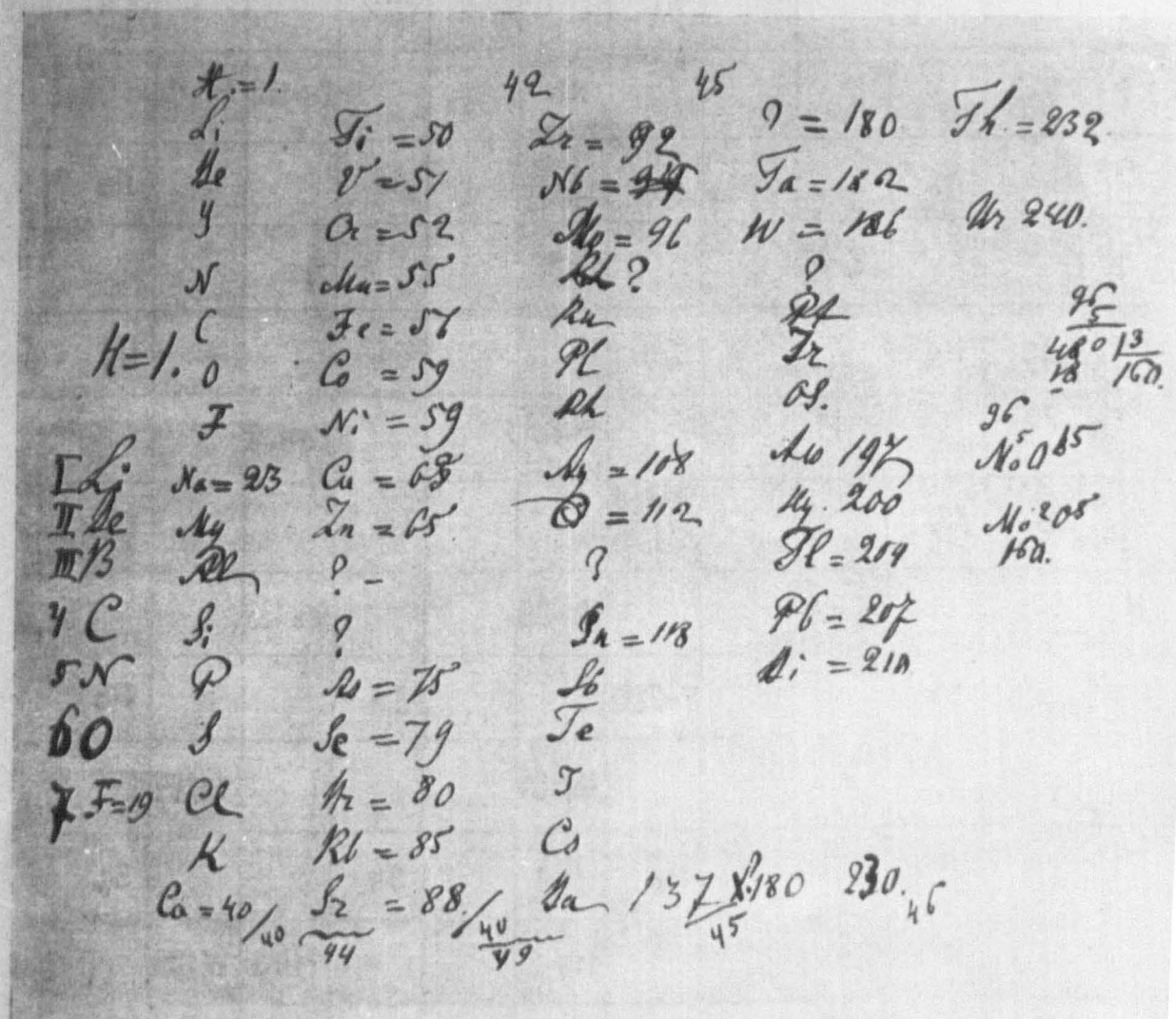


Фотокопия 10. Набросок короткой таблицы элементов с дальнейшими исправлениями атомных весов и перестановкой некоторых элементов.

Table 17 (M11)(a)

H=1				Fe			Pl			Os
				Co			Ru?			Ir
				Ni			Rh			Pt
		K			Rb			Cs=133		
Li	Na			Cu			Ag			Au
		Ca=40			Sr=88			Ba		
Be	Mg			Zn			Cd			Hg
		~~CeLaDi!!~~ ~~x45~~			Yt?3Yt?c? CeLaDi!!			Ce=138		
B	Al			~~CeLaDi~~ ~~Zn?68!~~ ~~Er?3?Co?~~			In			Tl
		Ti=50			Zr=90			?Ce=138		Th231
C	Si			?=72?!			Sn			Pb
		V			Nb=94				Ta182	
N	P			As			Sb			Bi
		Cr			Mo			?143	W186	U=240
O	S			Se			Te			
		Mn ↘			x98!! ↘			?145	x=190	
F	Cl			Br			J			
	1	2		3	4		5	6		

Table 17 (M11) (b).

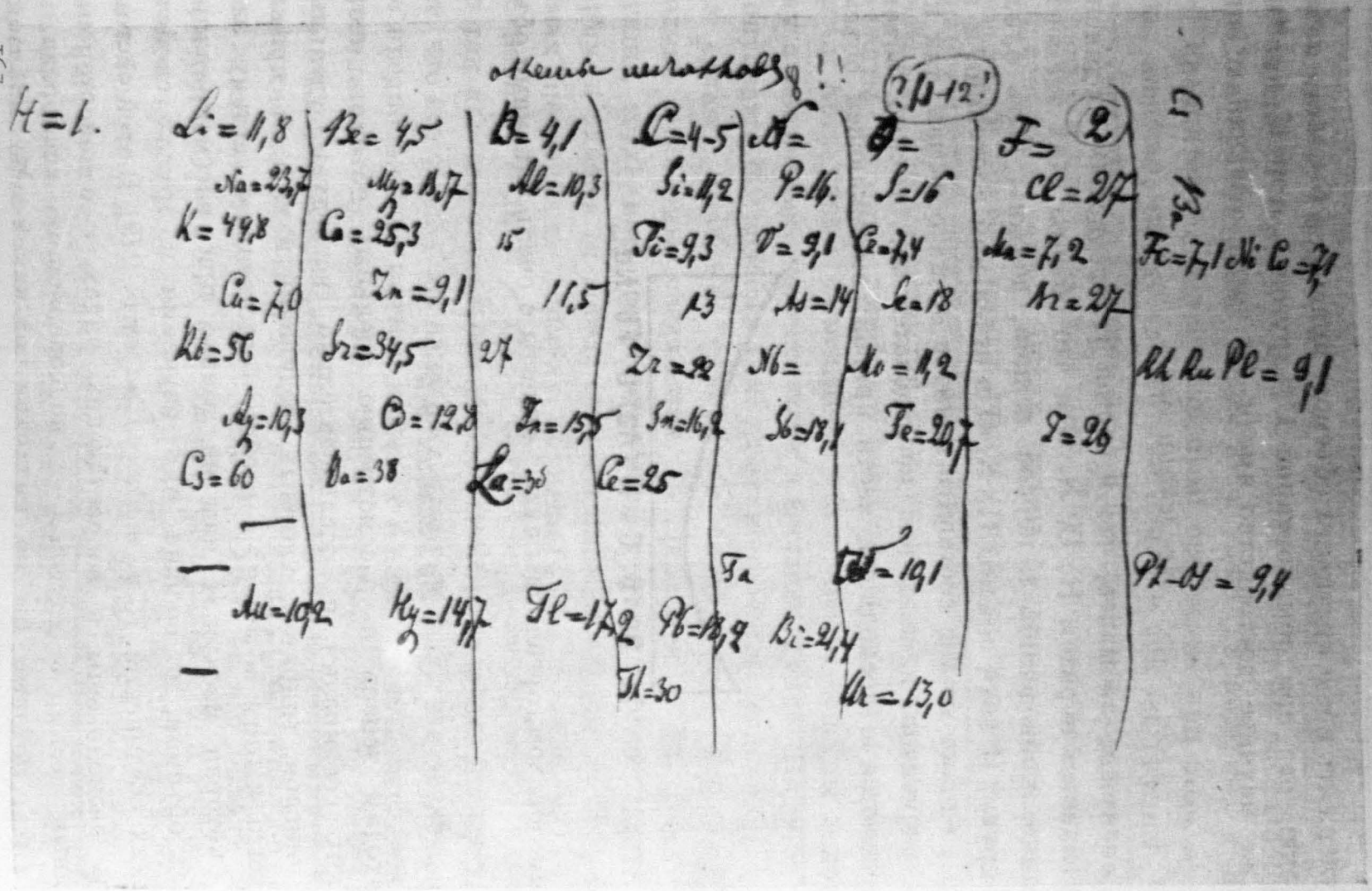


Фотокопия 14. Длинная таблица элементов с исправленными атомными весами (ум.)

Table 18 (M12)(a)

	H=1				
	Li	Ti=50	Zr=92	?=180	Th=232
	Be	V=51	Nb=94	Ta=182	
	J	Cr=52	Mo=96	W=186	Ur 240
	N	Mn=55	~~Rh~~ ?	?	
	C	Fe=56	Ru	Pt	
H=1	O	Co=59	Pl	Ir	
	F	Ni=59	Rh	Os	
I Li	Na=23	Cu=63	Ag=108	Au 197	
II Be	Mg	Zn=65	Cd=112	Hg 200	
III B	Al	?-	?	Tl=204	
4 C	Si	?	Sn=118	Pb=207	
5 N	P	As=75	Sb	Bi=210	
6 O	S	Se=79	Te		
7 F=19	Cl	Br=80	J		
	K	Rb=85	Cs		
	Ca=40	Sr=88	Ba 137	x?180	230

Table 18 (M12) (b).



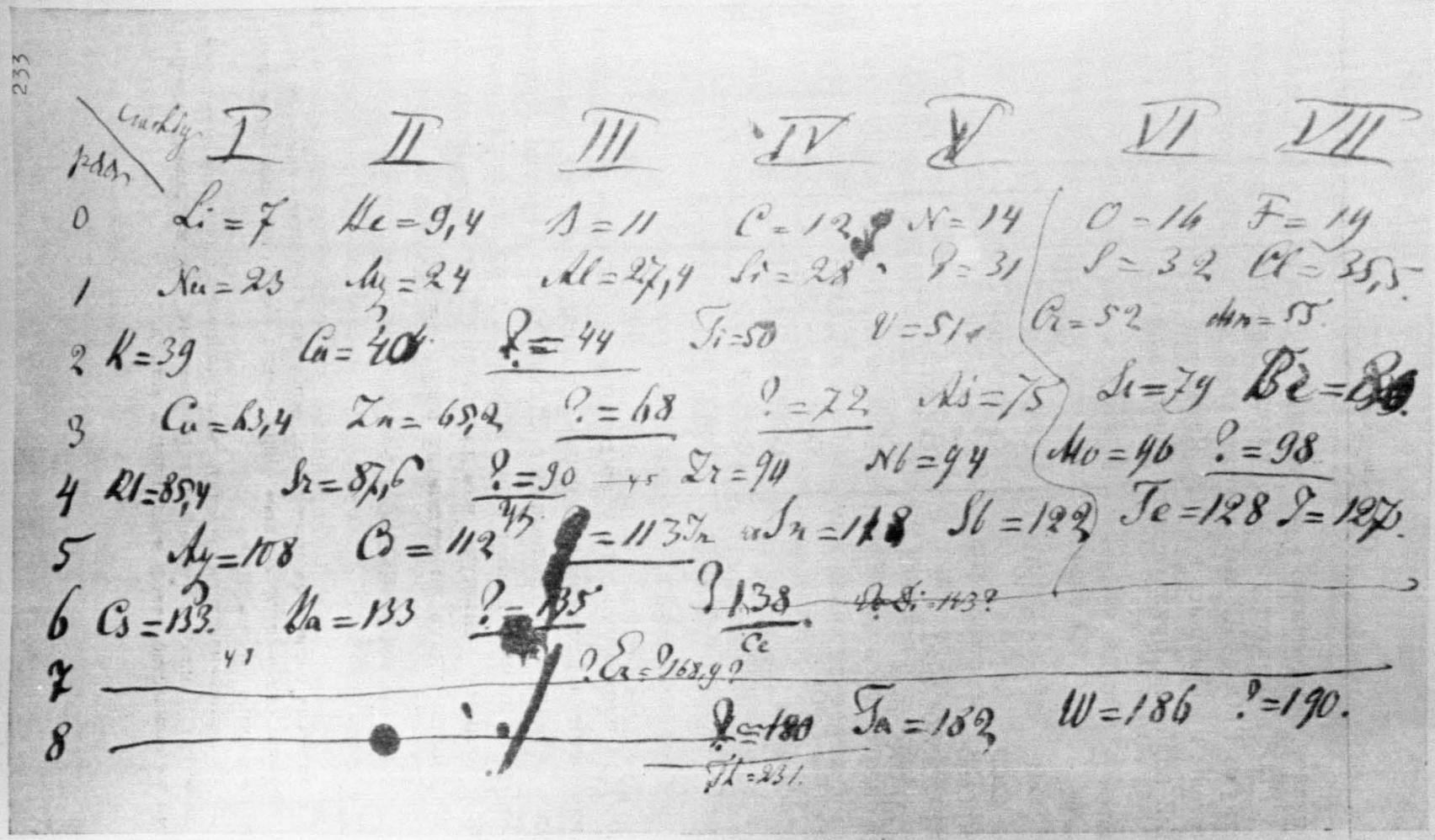
Фотокопия 24. Автограф таблицы элементов «Объемы металлов с исправленными атомными объемами» (осень 1870 г.)

Table 19 (M13)(a)

Table 19(M13) (b).

The volumes of metals

					8?!	(?11-12?)	(12)	
H=1	Li=11·8	Be=4·5	B=4·1	C=4·5	N=	O=	F=	
	Na=23·7	Mg=13·7	Al=10·3	Si=11·2	P=16	S=16	Cl=27	
	K=44·8	Ca=25·3	15	Ti=9·3	V=9·1	Cr=7·4	Mn=7·2	Fe=7·1 NiCo=7·1
	Cu=7·0	Zn=9·1	11·5	13	As=14	Se=18	Br=27	
	Rb=56	Sr=34·5	27	Zr=22	Nb=	Mo=11·2		Rh Ru Pl=9·1
	Ag=10·3	Cd=12·8	In=15·5	Sn=16·2	Sb=18·1	Te=20·7	J=26	
	Cs=60	Ba=38	La=30	Ce=25				
	—							
	—				Ta	W=10·1		Pt-Os=9·4
	Au=10·2	Hg=14·7	Tl=17·2	Pb=18·2	Bi=21·4			
	—			Th=30		Ur=13·0		



Фотокопия 11. Автограф «короткой» таблицы элементов с нумерацией рядов и столбцов, но без VIII группы

Table 20 (M14)(a)

series \ column	I	II	III	IV	V	VI	VII
0		Li=7	Be=9·4	B=11	C=12	N=14	O=16	F=19
1		Na=23	Mg=24	Al=27·4	Si=28	P=31	S=32	Cl=35·5
2	K=39	Ca=40	?=44	Ti=50	V=51	Cr=52	Mn=55
3		Cu=63·4	Zn=65·2	?=68	?=72	As=75	Se=79	Br=80
4	Rb=85·4	Sr=87·6	?=90 (Yt)	Zr=90	Nb=94	Mo=96	?=98
5		Ag=108	Cd=112	?=113 In	Sn=118	Sb=122	Te=128	J=127
6	Cs=133	Ba=133	?=135 (La)	?138 (Ce)	?Di=143?		
7	?Er=?168·9?						
8			?=180	Ta=182	W=186	?=190	
				Th=231			

Table 20 (M14) (b).

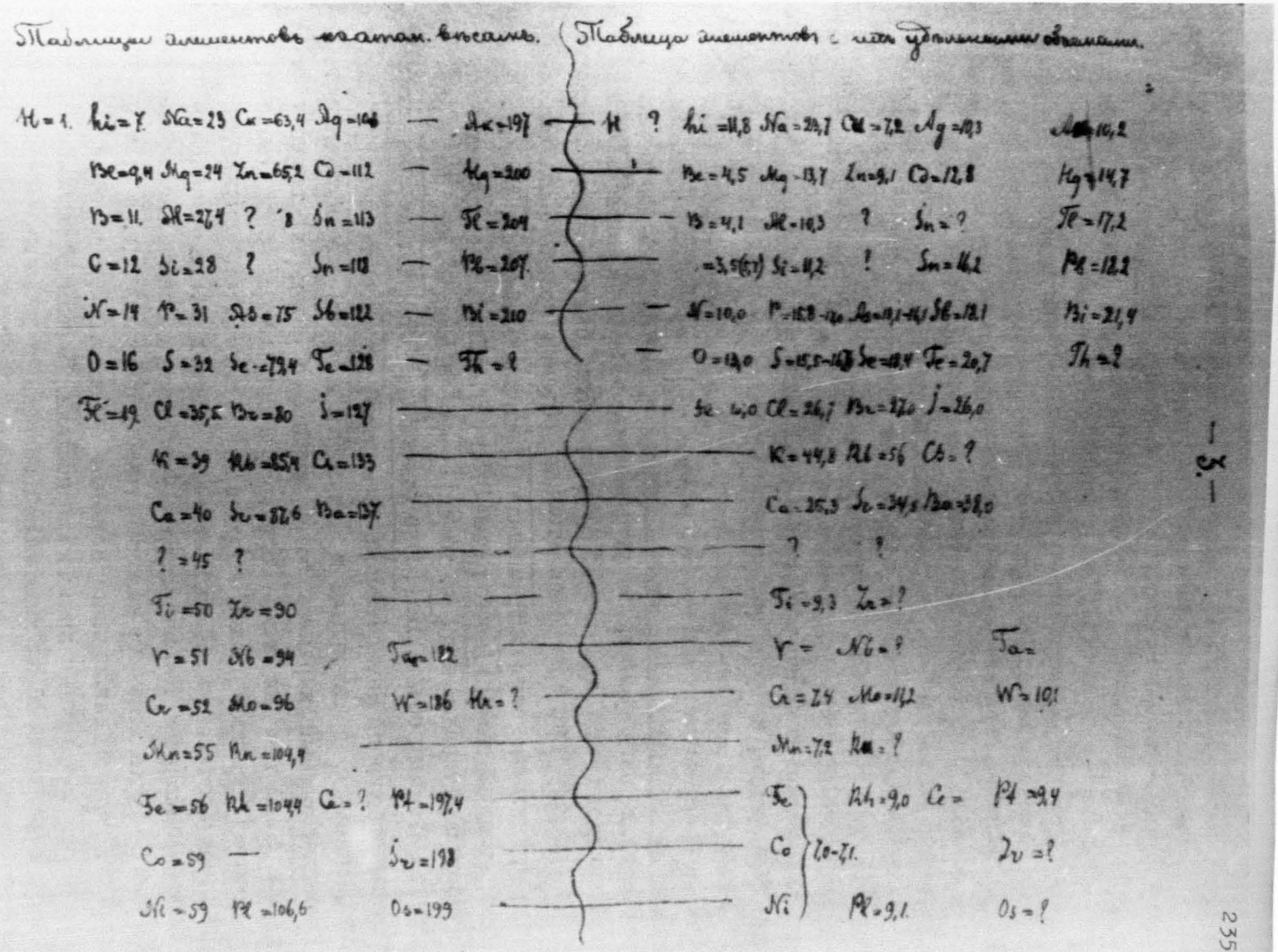


Table 21 (L1)(a)

Фотокопия 31. «Таблица элементов по атомным весам» и «Таблица элементов с их удельными объемами» (а).

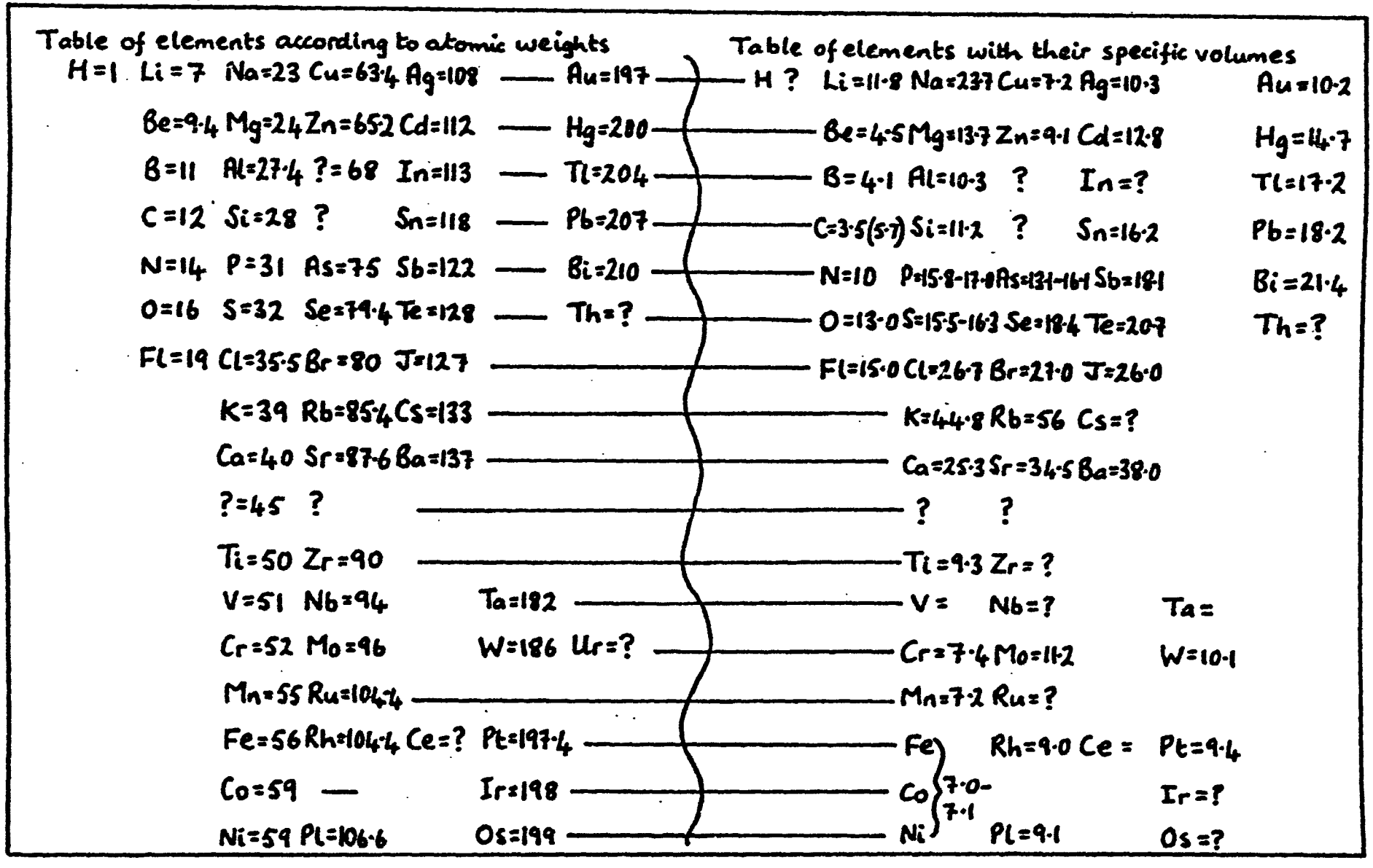


Table of elements according to atomic weights
H=1 Li=7 Na=23 Cu=63·4 Ag=108 —— Au=197
Be=9·4 Mg=24 Zn=65·2 Cd=112 —— Hg=200
B=11 Al=27·4 ?=68 In=113 —— Tl=204
C=12 Si=28 ? Sn=118 —— Pb=207
N=14 P=31 As=75 Sb=122 —— Bi=210
O=16 S=32 Se=79·4 Te=128 —— Th=?
Fl=19 Cl=35·5 Br=80 J=127
K=39 Rb=85·4 Cs=133
Ca=40 Sr=87·6 Ba=137
?=45 ?
Ti=50 Zr=90
V=51 Nb=94 Ta=182
Cr=52 Mo=96 W=186 Ur=?
Mn=55 Ru=104·4
Fe=56 Rh=104·4 Ce=? Pt=197·4
Co=59 — Ir=198
Ni=59 Pl=106·6 Os=199
Table of elements with their specific volumes
H ? Li=11·8 Na=23·7 Cu=7·2 Ag=10·3 Au=10·2
Be=4·5 Mg=13·7 Zn=9·1 Cd=12·8 Hg=14·7
B=4·1 Al=10·3 ? In=? Tl=17·2
C=3·5(5·7) Si=11·2 ? Sn=16·2 Pb=18·2
N=10 P=15·8-17·0 As=13·1-16·1 Sb=18·1 Bi=21·4
O=13·0 S=15·5-16·3 Se=18·4 Te=20·7 Th=?
Fl=15·0 Cl=26·7 Br=21·0 J=26·0
K=44·8 Rb=56 Cs=?
Ca=25·3 Sr=34·5 Ba=38·0
? ?
Ti=9·3 Zr=?
V= Nb=? Ta=
Cr=7·4 Mo=11·2 W=10·1
Mn=7·2 Ru=?
Fe Rh=9·0 Ce= Pt=9·4
Co 7·0-7·1 Ir=?
Ni Pl=9·1 Os=?

Table 21 (Li) (b).

Фотокопия 17. Верхняя часть короткой таблицы элементов (УВ.)

Table 22 (M15)(a)

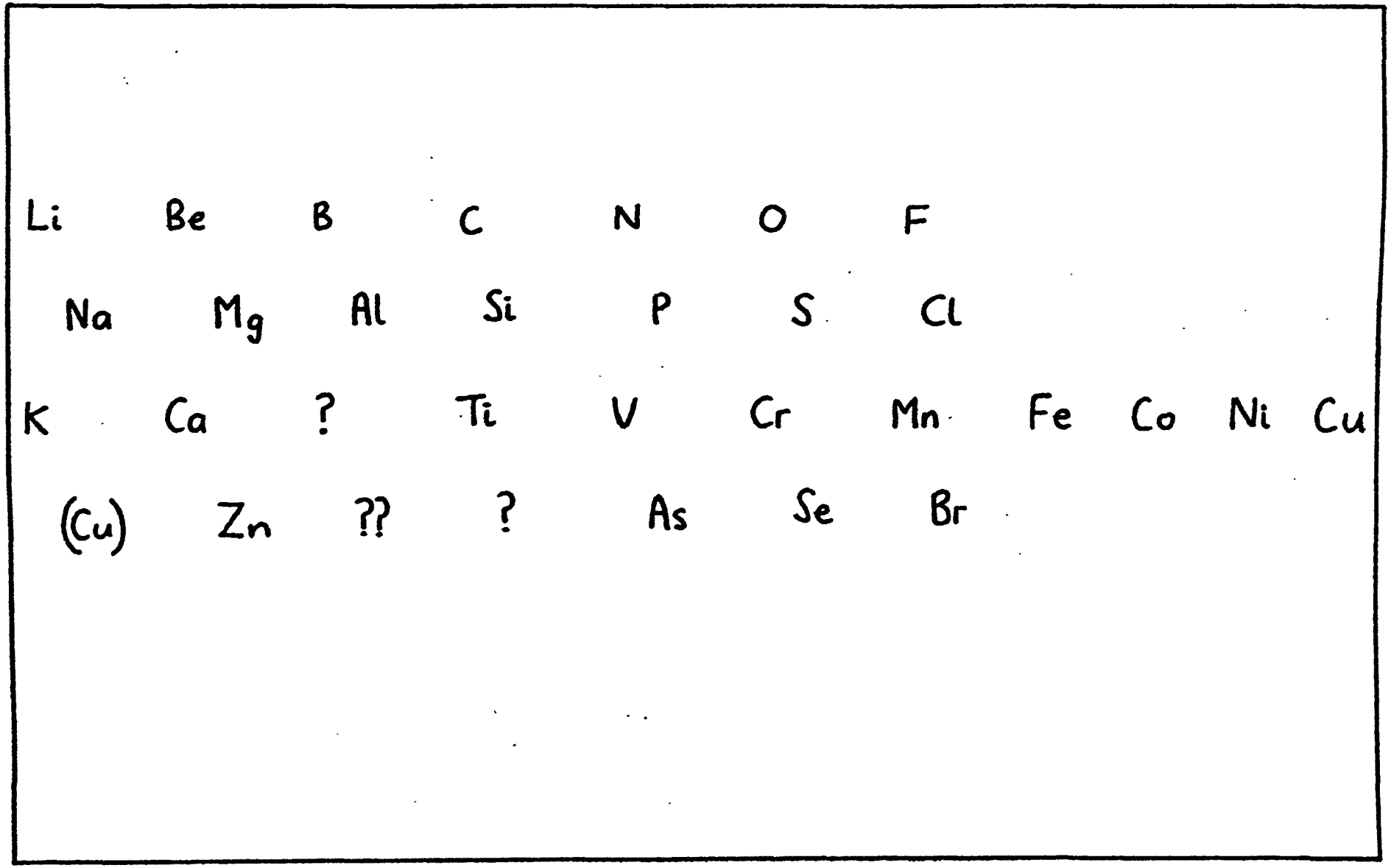
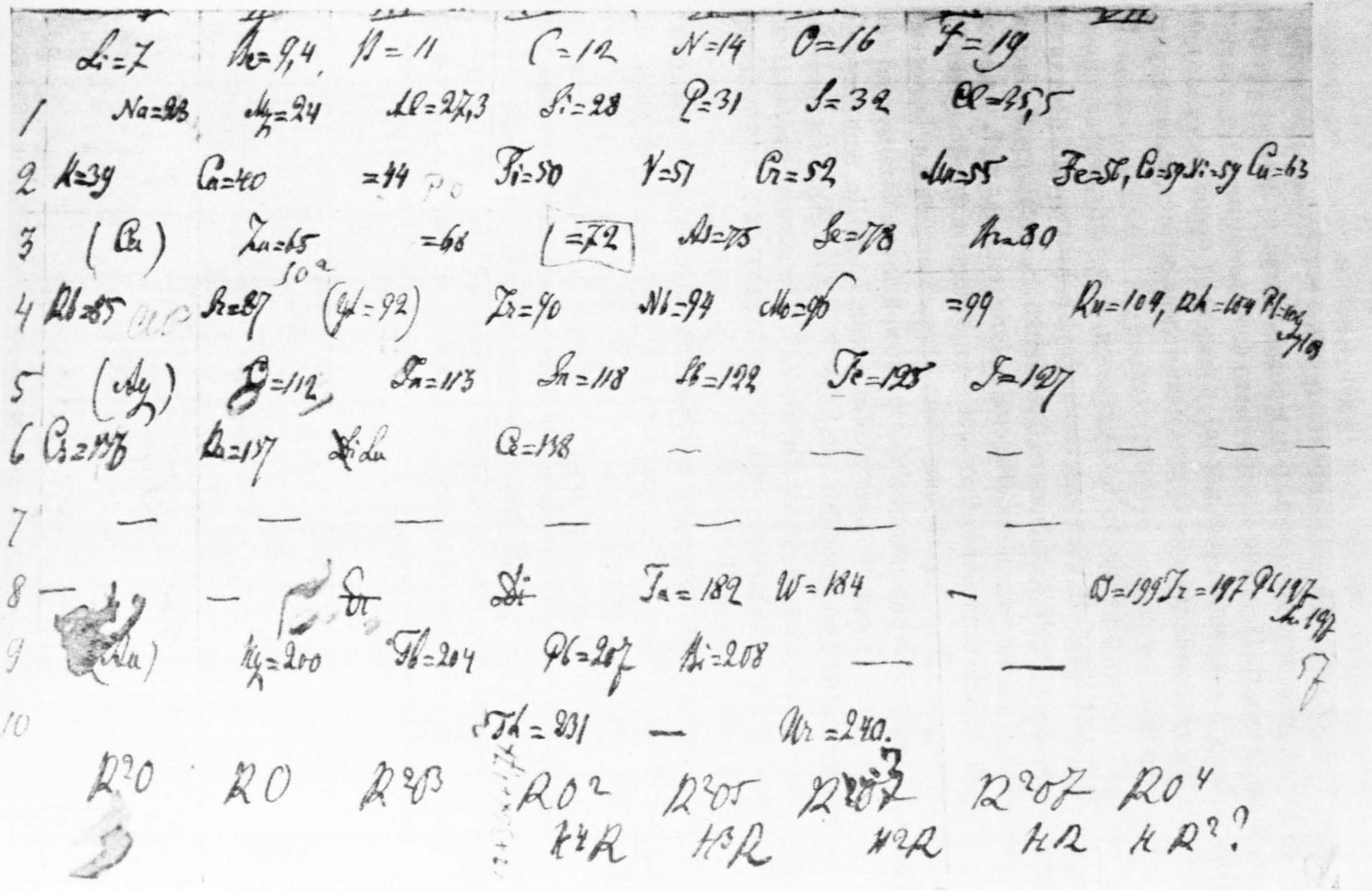


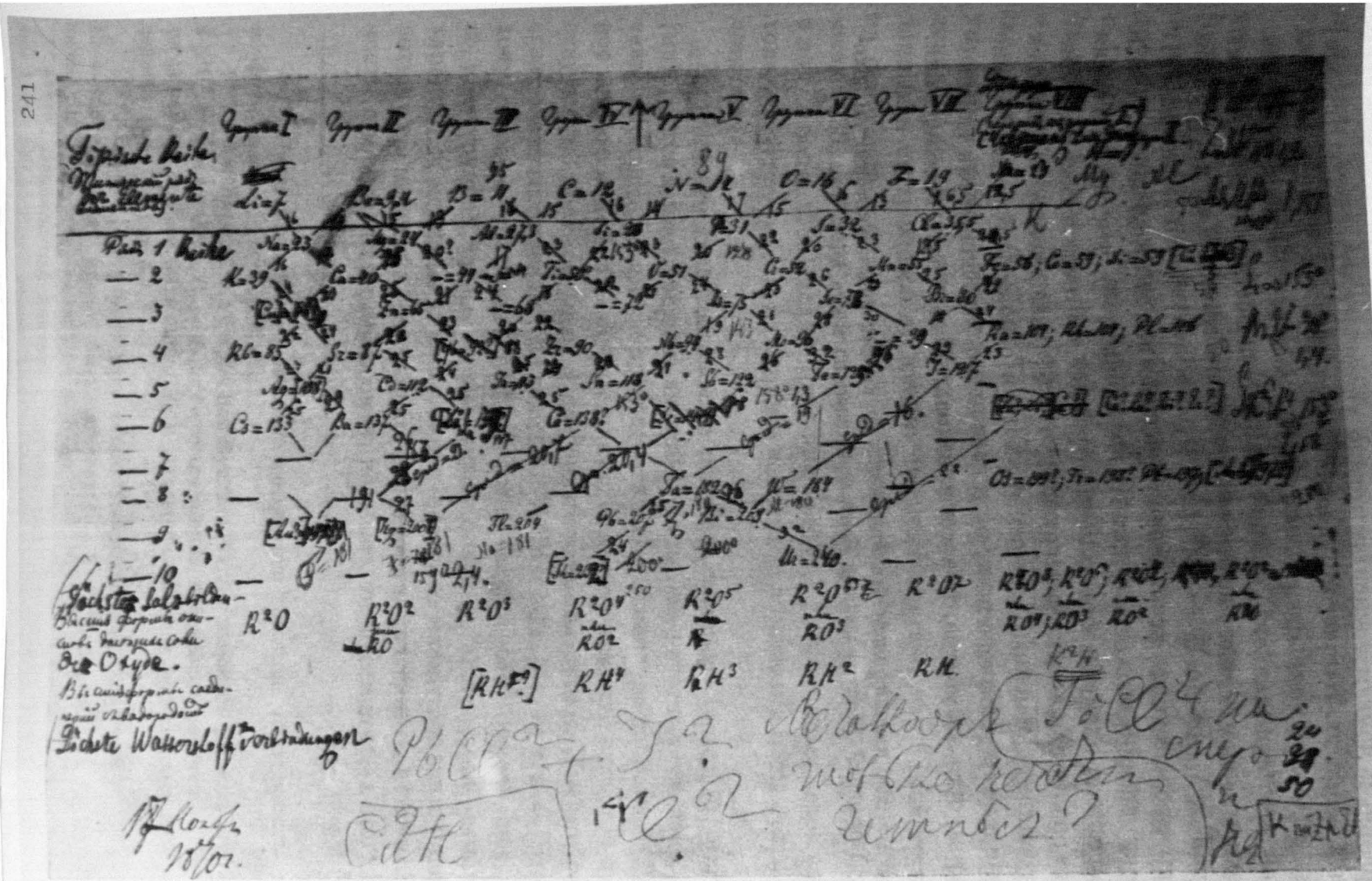
Table 22 (M15) (b).



Фотокопия 18. Автограф короткой таблицы элементов (с 8-й группой) (ум.)

Table 23 (№16) (a).

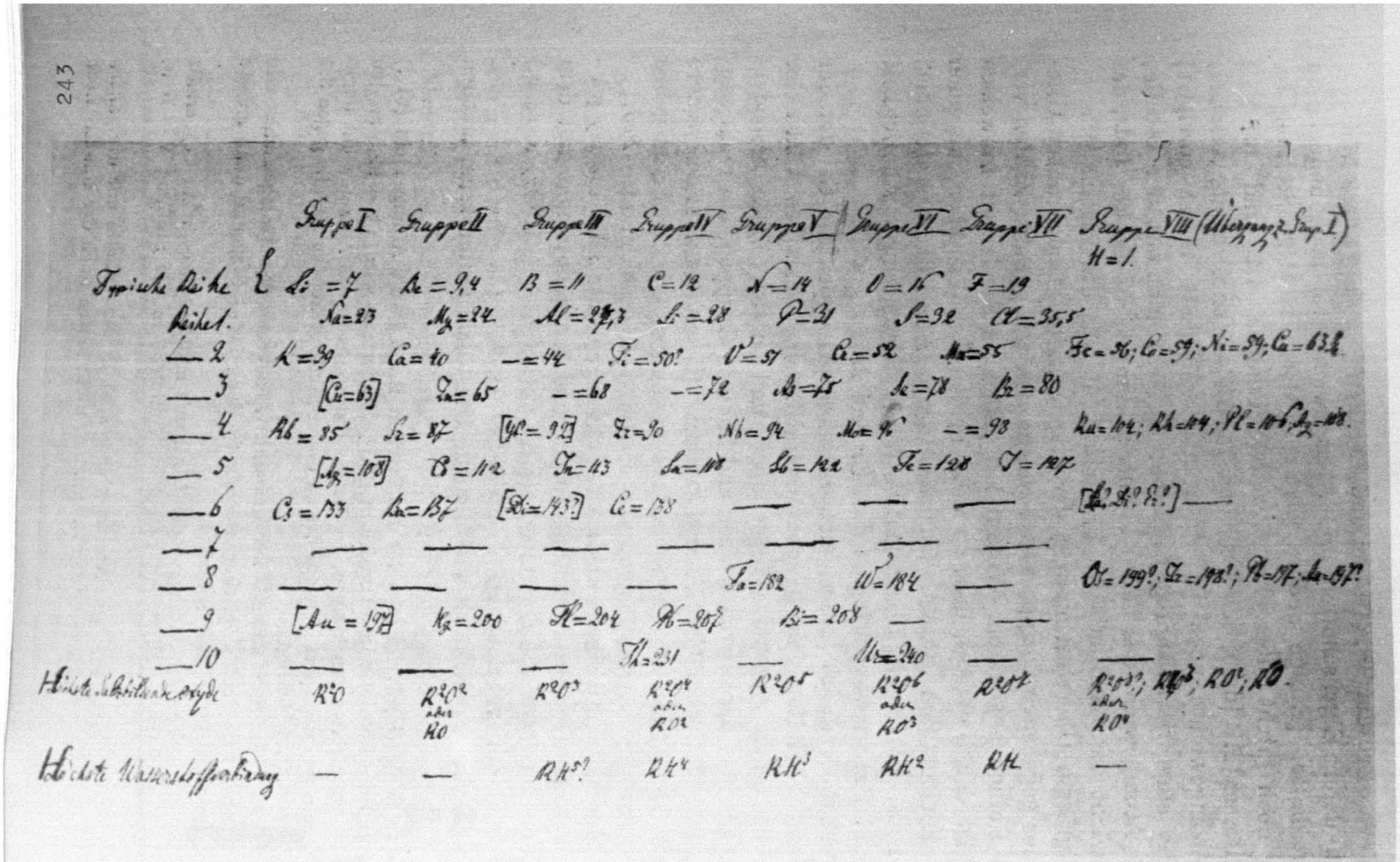
	I	II	III	IV	V	VI	VII	VIII
	Li=7	Be=9·4	B=11	C=12	N=14	O=16	F=19	
1	Na=23	Mg=24	Al=27·3	Si=28	P=31	S=32	Cl=35·5	
2	K=39	Ca=40	=44	Ti=50	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
3	(Cu)	Zn=65	=68	=72	As=75	Se=78	Br=80	
4	Rb=85	Sr=87	(Yt=92)	Zr=90	Nb=94	Mo=96	=99	Ru=104, Rh=104, Pl=106, Ag=108
5	(Ag)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
6	Cs=133	Ba=137	~~Di~~ La	Ce=138	—	—	—	— — —
7	—	—	—	—	—	—	—	
8	—	—	Er	Di	Ta=182	W=184	—	Os=199, Ir=197, Pt=197, Au 197
9	(Au)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
10	R^2O	RO	R^2O^3	Th=231 $12+36x+17x^3$ RO^2 H^4R	— R^2O^5 H^3R	Ur=240 RO^3 H^2R	R^2O^7 HR	RO^4 HR^2?



Фотокопия 20. **Черновик таблицы «Системы элементов» с расчетами атомных весов (ум.)**

	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII (transition to Group I)	
Typical series of elements	Li=7	Be=9·4	B=11	C=12	N=14	O=16	F=19	Na=23	Mg H=1 Al
Series 1	Na=23	Mg=24	Al=27·3	Si=28	P=31	S=32	Cl=35·5	K	
– 2	K=39	Ca=40	–=44	Ti=50?	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59	[Cu?=63]
– 3	[Cu]	Zn=65	–=68	–=72	As=75	Se=78	Br=80		
– 4	Rb=85	Sr=87	88	Zr=90	Nb=94	Mo=96	–=99	Ru=104, Rh=104, Pl=106	
– 5	Ag=[108]	Cd=112	In=113	Sn=118	Sb=122	Te=125?	J=127		
– 6	Cs=133	Ba=137	[Di=139?] La 137	Ce=138?	–	–	–	[Ce? La? Di? Er?]	
– 7	–	163	–	–	–	–	–		
– 8	–	191	–	–	Ta=182	W=184	–	Os=199?, Ir=198? Pt=197,	[Au?=197?]
– 9	[Au?]	[Hg=200?]	Tl=204	Pb=207	Bi=208	–	–		
– 10	–	–	–	[Th=232?]	–	Ur=240	–	–	
Highest salt-forming oxides	R^2O	R^2O^2 or RO	R^2O^3	R^2O^4 or RO^2	R^2O^5	R^2O^6 or RO^3	R^2O^7	R^2O^8; R^2O^6; R^2O^4; R^2O^2 or RO^4 or RO^3 or RO^2 or RO	
Highest forms of hydrogen compounds		[RH^5?]	RH^4	RH^3	RH^2	RH	R^2H		

Table 24(M17) (b).

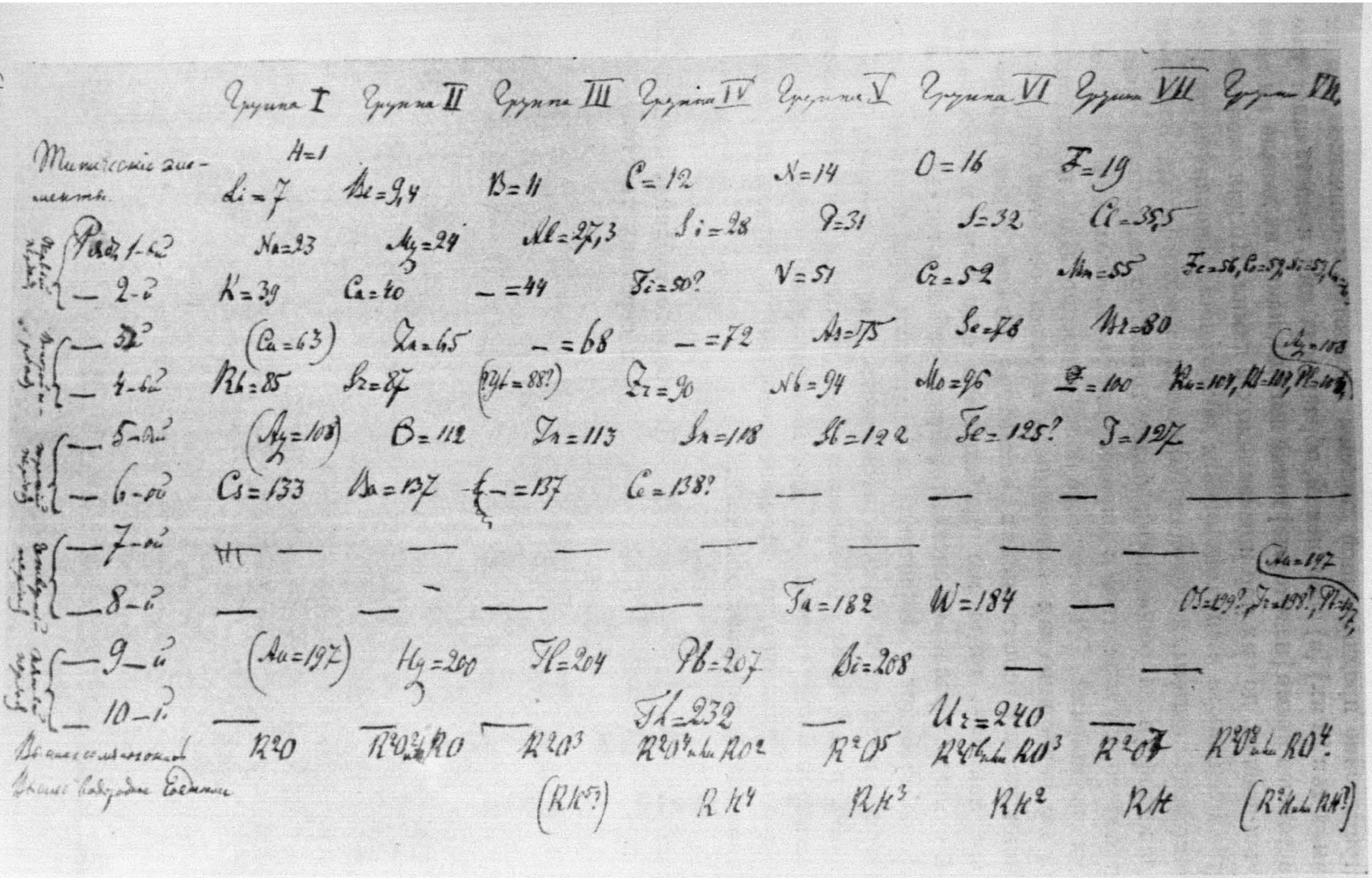


Фотокопия 22. **Автограф таблицы «Системы элементов» для немецкой статьи (ум.)**

Table 25 (M18)(a)

	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII (transition to Gp. I)
Typical series	Li=7	Be=9·4	B=11	C=12	N=14	O=16	F=19	H=1
Series 1	Na=23	Mg=24	Al=27·3	Si=28	P=31	S=32	Cl=35·5	
— 2	K=39	Ca=40	-=44	Ti=50?	V=51	Cr=52	Mn=55	Fe=56; Co=59; Ni=59; Cu=63
— 3	[Cu=63]	Zn=65	-=68	-=72	As=75	Se=78	Br=80	
— 4	Rb=85	Sr=87	[Yt?=92?]	Zr=90	Nb=94	Mo=96	-=98	Ru=104; Rh=104; Pl=106; Ag=108
— 5	[Ag=108]	Cd=112	In=113	Sn=118	Sb=122	Te=128	J=127	
— 6	Cs=133	Ba=137	[Di=143?]	Ce=138	—	—	—	[La? Di? Er?] ——
— 7	—	—	—	—	—	—	—	
— 8	—	—	—	—	Ta=182	W=184	—	Os=199?; Ir=198? Pt=197; Au=197?
— 9	[Au=197]	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
— 10	—	—	—	Th=231	—	Ur=240	—	——
Highest salt-forming oxides	R^2O	R^2O^2 or RO	R^2O^3	R^2O^4 or RO^2	R^2O^5	R^2O^6 or RO^3	R^2O^7	R^2O^8?; RO^3; RO^2; RO or RO^4
Highest hydrogen compounds	—	—	RH^5?	RH^4	RH^3	RH^2	RH	—

Table 25 (M18) (b).



Фотокопия 24. **Автограф таблицы «Естественная система элементов» (ум.)**

Table 26 (M19)(a)

	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
	H=1							
Typical elements	Li=7	Be=9·4	B=11	C=12	N=14	O=16	F=19	
First period, 1st series	Na=23	Mg=24	Al=27·3	Si=28	P=31	S=32	Cl=35·5	
First period, 2nd series	K=39	Ca=40	-=44	Ti=50?	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
Second period, 3rd series	[Cu=63]	Zn=65	-=68	-=72	As=75	Se=78	Br=80	
Second period, 4th series	Rb=85	Sr=87	[?Yt=88?]	Zr=90	Nb=94	Mo=96	-=100	Ru=104, Rh=104, Pt=106, Ag=108
Third period, 5th series	[Ag=108]	Cd=112	In=113	Sn=118	Sb=122	Te=125?	J=127	
Third period, 6th series	Cs=133	Ba=137	-=137	Ce=138?	—	—	—	———
Fourth period, 7th series	—	—	—	—	—	—	—	
Fourth period, 8th series	—	—	—	—	Ta=182	W=184	—	Os=199?, Ir=198?, Pt=197, Au=197
Fifth period, 9th series	[Au=197]	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
Fifth period, 10th series	—	—	—	Th=232	—	Ur=240	—	
Highest saline oxide	R^2O	R^2O^2 or RO	R^2O^3	R^2O^4 or RO^2	R^2O^5	R^2O^6 or RO^3	R^2O^7	R^2O^8 or RO^4
Highest hydrogen compound		[RH^5?]	RH^4	RH^3	RH^2	RH	[R^2H or RH?]	

Table 26 (M19) (b).

Table27 (I.2)

H=1

R^2O	R^2O^2	R^2O^3	$[R^2O^4]$ RO^2 RH^4	R^2O^5 RH^3	$[R^2O^6]$ RO^3 RH^2	R^2O^7 RH				
Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	Na=23			
Na=23	Mg=24	Al=27.4	Si=28	P=31	S=32	Cl=35.5				
K=39	Ca=40	—	Ti=50	V=51	Cr=52	Mn=55	Fe=56	Co=59	Ni=59	Cu=63.4
(Cu)	Zn=65.2	—	—	As=75	Se=78	Br=80				
Rb=85	Sr=87	—	Zr=90	Nb=94	Mo=96	Rh=104	Ru=104	Pl=106	—	Ag=108
(Ag)	Cd=112	Ur=116	Sn=118	Sb=122	Te=128	I=127				
Cs=133	Ba=137		Ce=138							
				Ta=182	W=186	Os=199	Ir=199	Pt=197	Au=197	
(Au)	Hg=200	Tl=204	Pb=207							
Tl=204	Pb=207			Bi=210						Hg=200
			Th=231							

Фотокопия 25. Естественная система элементов из литографированного издания лекций Д. И. Менделеева по химии (1870/71 г.)

Table 28 (L3)(a)

Table 28 (Li) (%)

	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	R_2O_8
0	Li —	Be —	B —	C —	N —	O —	Fl —	
1	— Na	— Mg	— Al	— Si	— P	— S	— Cl	
2	K —	Ca —	? —	Ti —	V —	Cr —	Mn —	Fe, Co, Ni; Cu
3	— (Cu)	— Zn	— ?	— ?	— As	— Se	— Br	
4	Rb —	Sr —	? —	Zr —	Nb —	Mo —	? —	Ru, Rh, Pd, Ag
5	— (Ag)	— Cd	— In	— Sn	— Sb	— Te	— J	
6	Cs —	Ba —	(La, Di)? —	Ce —	? —	? —	? —	
7	— ?	— ?	— ?	— ?	— ?	— ?	— ?	
8	? —	? —	? —	? —	Ta —	W —	? —	Os, Ir, Pt, Au
9	— (Au)	— Hg	— Tl	— Pb	— Bi	— ?	— ?	
10	? —	? —	? —	Th —	? —	Ur —	? —	

Фотокопия 30. **Пометки Д. И. Менделеева на обороте таблицы «Естественной системы элементов»** (ум.)

Table 29 (M20)(a)

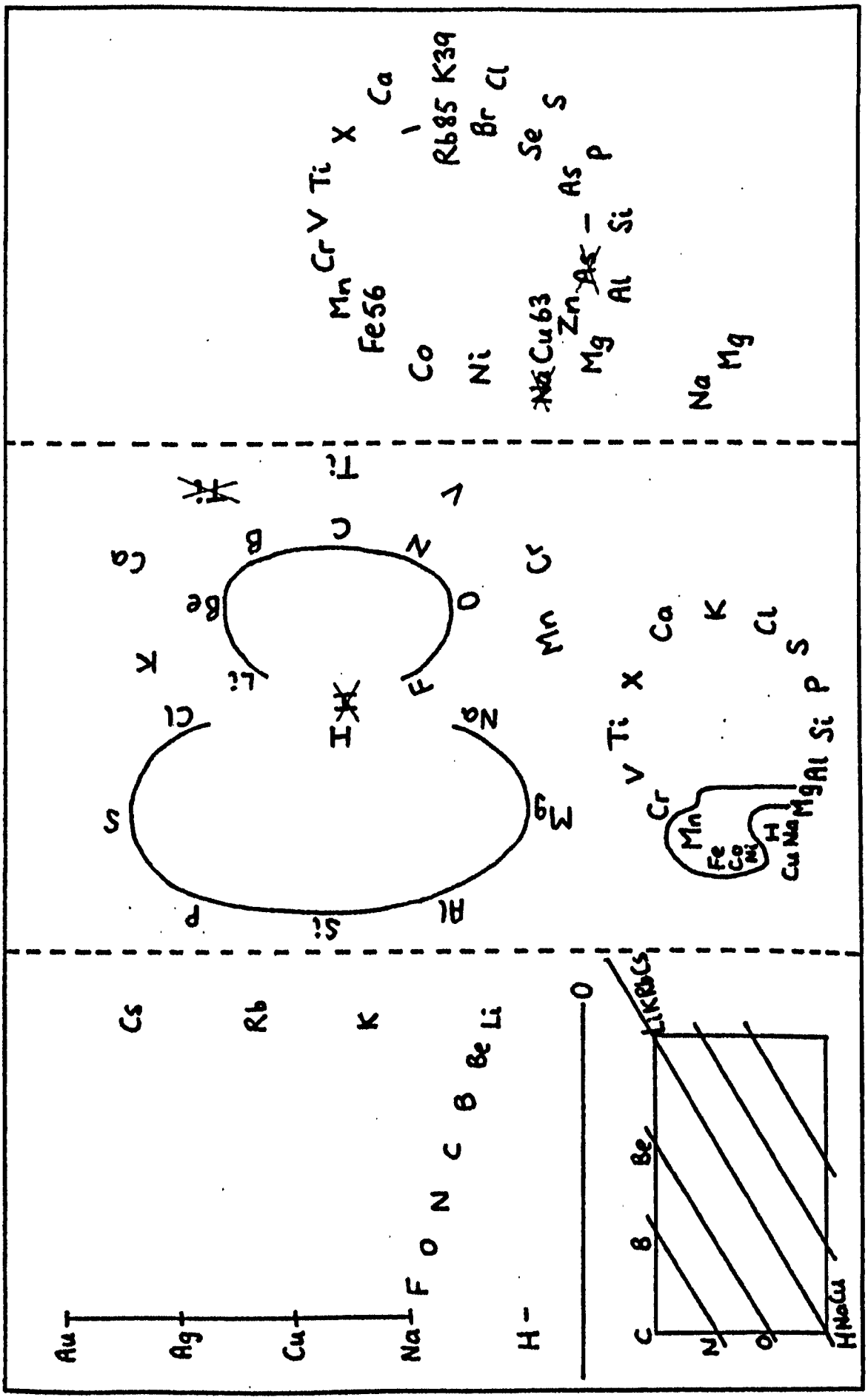


Table 29 (M20) (b).

Table 30 (p7)

[31]		Группа I	Группа II	Группа III	Группа IV	Группа V	Группа VI	Группа VII	Группа VIII. Переход к группе I
		H = 1							
Типические элементы		Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
Первый период	Ряд 1-й	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
	— 2-й	K = 39	Ca = 40	— = 44	Ti = 50?	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63
Второй период	— 3-й	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
	— 4-й	Rb = 85	Sr = 87	(?Yt = 88?)	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 104, Ag = 108
Третий период	— 5-й	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 128?	J = 127	
	— 6-й	Cs = 133	Ba = 137	— = 137	Ce = 138?	—	—	—	— —
Четвертый период	— 7-й	—	—	—	—	—	—	—	
	— 8-й	—	—	—	—	Ta = 182	W = 184	—	Os = 199?, Ir = 198? Pt = 197?, Au = 197
Пятый период	— 9-й	(Au = 197)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
	— 10-й	—	—	—	Th = 232	—	Ur = 240	—	
Высшая соляная окись		R^2O	R^2O^2 или RO	R^2O^3	R^2O^4 или RO^2	R^2O^5	R^2O^6 или RO^3	R^2O^7	R^2O^8 или RO^4
Высшее водородное соединение				(RH^5?)	RH^4	RH^3	RH^2	RH	—

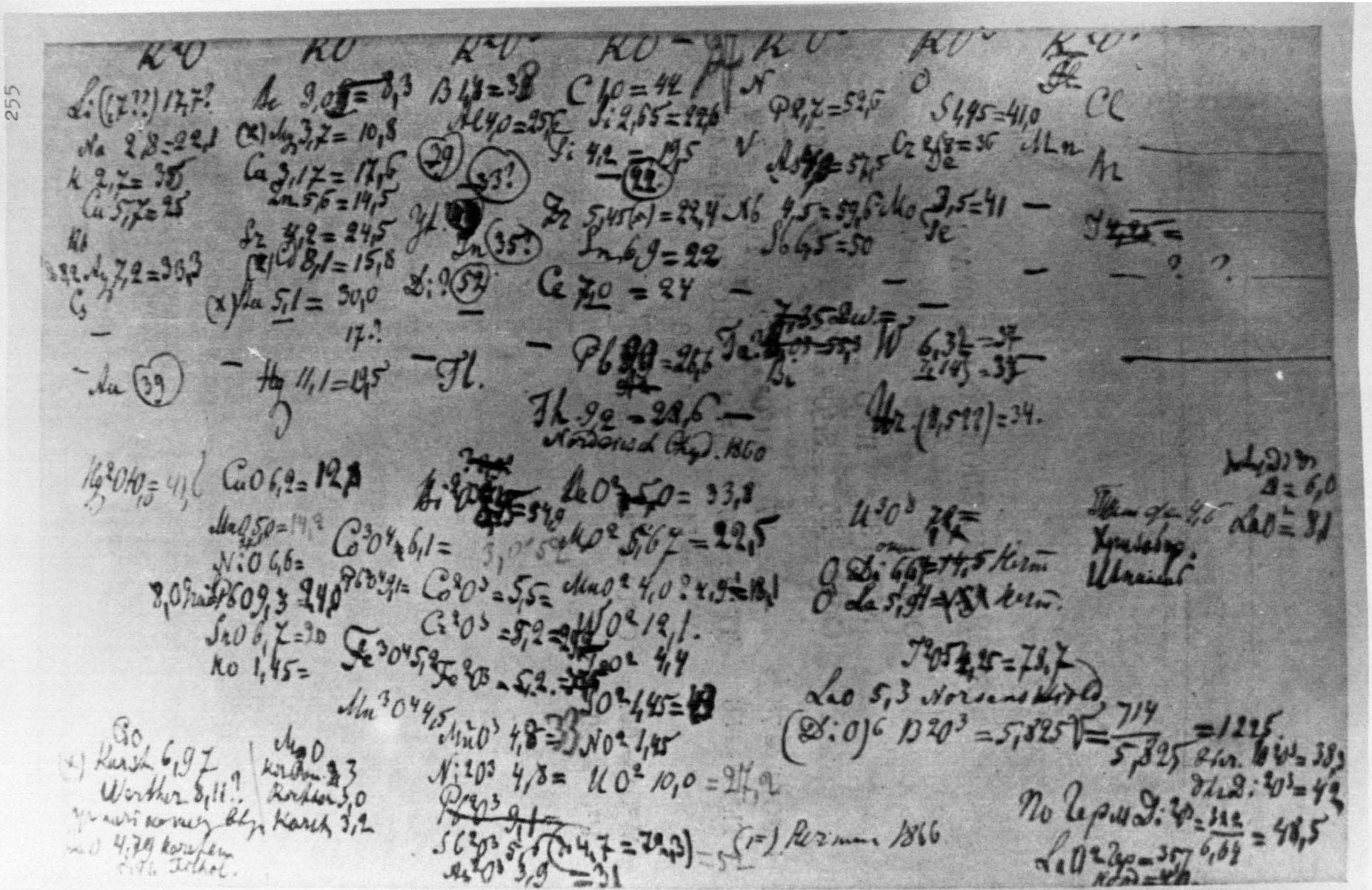
Li	Be	B	C	N	O	F					H Na	Mg	Al	Si	P	S	Cl
K	Ca	—	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	—	—	As	Se	Br	
Rb	Sr	Yt?	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	
Cs	Ba	Di?	Ce	—	—	—	—	—	—	—	—	—	—	—	—	—	
—	—	Er?	La?	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	
—	—	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	—	

Естественная система элементов Д. Менделеева
Группа I. R'O
Группа II. R'O или RO
Группа III. R'O'
Группа IV. RH' R'O' или RO'
Группа V. RH' R'O' или RO'
Группа VI. RH R'O'
Группа VII. R'H R'O'
Группа VIII. (переход 8) R'O' или RO'
Ряды
Периоды 1-й. Периоды 2-й. Периоды 3-й. Периоды 4-й. Периоды 5-й
H=1
Li=7
Be=9,4
B=11
C=12
N=14
O=16
F=19
Na=23
Mg=24
Al=27,3
Si=28
P=31
S=32
Cl=35,5
K=39
Ca=40
Ti=48(?)
V=51
Cr=52
Mn=55
Fe=56
Co=59
Ni=59
Cu=63
Rb=85
Sr=87
Zr=90
Nb=94
Mo=96
Ru=104
Rh=104
Pd=106
Ag=108
Cs=133
Ba=137
Di=138—La=(180?)
Ce=140
Ta=182
W=184
Os=193
Ir=195
Pt=197
Au=197
Tl=204
Pb=207
Bi=208
Th=231
U=240
Hg=200
In=113
Sn=118
Sb=122
Te=125(?)
I=127
Cd=112
Zn=65
Ur=75
Se=78
Br=80
Ta=182
Ti=48(?)
Di=138—La=(180?)
Ce=140
Er=178
La=180
Yt=88
Ur=75
Di=95
Ce=92
Th=231
U=240
Hg=200
Tl=204
Pb=207
Bi=208
Ta=182
W=184
Os=193
Ir=195
Pt=197
Au=197
Cd=112
In=113
Sn=118
Sb=122
Te=125(?)
I=127
Ag=108
Pd=106
Rh=104
Ru=104
Mo=96
Nb=94
Zr=90
Sr=87
Rb=85

Table 33 (P10)

СИСТЕМА ЭЛЕМЕНТОВ

	Группа I	Группа II	Группа III	Группа IV	Группа V	Группа VI	Группа VII	Группа VIII (переход к группе I)
Типический ряд	H = 1 Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
Ряд 1	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
» 2	K = 39	Ca = 40	— = 44	Ti = 50?	V = 51	Cr = 52	Mn = 55	Fe = 56; Co = 59; Ni = 59; Cu = 63
» 3	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
» 4	Rb = 85	Sr = 87	(Yt? = 92?)	Zr = 90	Nb = 94	Mo = 96	— = 98	Ru = 104; Rh = 104; Pl = 106; Ag = 108
» 5	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 128?	J = 127	
» 6	Cs = 133	Ba = 137	(Di = 143?)	Ce = 138	—	—	—	(La? Di? Er?) ————
» 7	—	—	—	—	—	—	—	
» 8	—	—	—	—	Ta = 182	W = 184	—	Os = 199?; Ir = 198?; Pt = 197?; Au = 197
» 9	(Au = 197)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
» 10	—	—	—	Th = 231	—	Ur = 240	—	—
Высшие формы окислов, дающих соли	R^2O	R^2O^2 или RO	R^2O^3	R^2O^4 или RO^2	R^2O^5	R^2O^6 или RO^3	R^2O^7	R^2O^8 или RO^4
Высшие формы соединений с водородом	—	—	RH^3?	RH^4	RH^3	RH^2	RH	—



Фотокопия 38. **Автограф короткой таблицы элементов с объемами окислов**

Table 34 (M21)(a)

R^2O	RO	R^2O^3	RO^2	R^2O^5	RO^3	R^2O^7
Li 17·7?	Be=8·3	B=38	C=44	N 27	O	F
Na=22·1	Mg=10·8	Al=25·6	Si=22·6	P=52·6	S=41·0	Cl
K=36	Ca=17·6	(39)	Ti=19·5	V	Cr=36	Mn ———
Cu=25	Zn=14·5	(33?)	(22)	As=57·5	Se	Br
Rb	Sr=24·5	Yt?(49)	Zr=22·4	Nb=59·6	Mo=41	— ———
Ag=33·3	Cd=15·8	In(35?)	Sn=22	Sb=50	Te	J
Cs	Ba=30·0	Di?(52)	Ce=24	—	—	— —??—
—	—17?	—	—	—	—	
—	—	—	—	Ta=	W}=37 =32	— ———
Au(39)	Hg=19·5	Tl	Pb=26·6	Bi	—	
			Th=28·6	—	Ur=34	

Table 34(M21) (b).

Tabelle I.

	Typische Elemente						
			K = 39	Rb = 85	Cs = 133	—	—
			Ca = 40	Sr = 87	Ba = 137	—	—
			—	?Yt = 88?	?Di = 138?	Er = 178?	—
			Ti = 48?	Zr = 90	Ce = 140?	?La = 180?	Th = 231
			V = 51	Nb = 94	—	Ta = 182	—
			Cr = 52	Mo = 96	—	W = 184	U = 240
			Mn = 55	—	—	—	—
			Fe = 56	Ru = 104	—	Os = 195?	—
			Co = 59	Rh = 104	—	Ir = 197	—
			Ni = 59	Pd = 106	—	Pt = 198?	—
H = 1	Li = 7	Na = 23	Cu = 63	Ag = 108	—	Au = 199?	—
	Be = 9,4	Mg = 24	Zn = 65	Cd = 112	—	Hg = 200	—
	B = 11	Al = 27,3	—	In = 113	—	Tl = 204	—
	C = 12	Si = 28	—	Sn = 118	—	Pb = 207	—
	N = 14	P = 31	As = 75	Sb = 122	—	Bi = 208	—
	O = 16	S = 32	Se = 78	Te = 125?	—	—	—
	F = 19	Cl = 35,5	Br = 80	J = 127	—	—	—

Table35(P11)

Tabelle II.

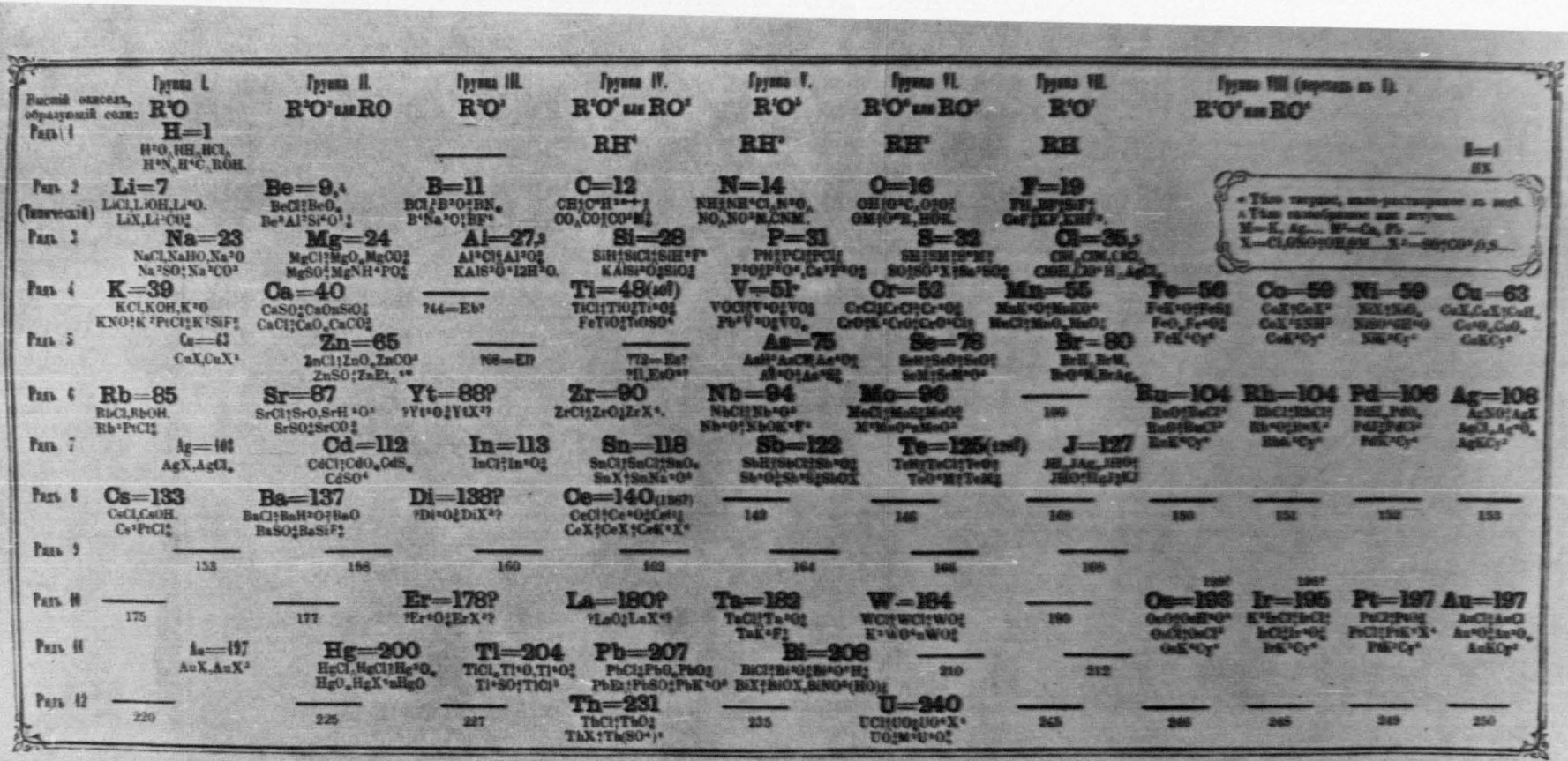
Reihen	Gruppe I. — R^1O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Table36(P12)

Table 37 (p 13)

[IV] ОПЫТ СИСТЕМЫ ЭЛЕМЕНТОВ, ОСНОВАННОЙ НА ИХ АТОМНОМ ВЕСЕ И ХИМИЧЕСКОМ СХОДСТВЕ

			K = 39	Rb = 85	Cs = 133	—	—
			Ca = 40	Sr = 87	Ba = 137	—	—
			—	? Yt = 88?	? Di = 138?	? Er = 178?	—
			Ti = 48?	Zr = 90	Ce = 140?	? La = 180?	Th = 231
			V = 51	Nb = 94	—	Ta = 182	—
			Cr = 52	Mo = 96	—	W = 184	U = 240
			Mn = 55	—	—	—	—
			Fe = 56	Ru = 104	—	Os = 195?	—
	типические элементы		Co = 59	Rh = 104	—	Ir = 197	—
			Ni = 59	Pd = 106	—	Pt = 198?	—
H = 1	Li = 7	Na = 23	Cu = 63	Ag = 108	—	Au = 199?	—
	Be = 9,4	Mg = 24	Zn = 65	Cd = 112	—	Hg = 200	—
	B = 11	Al = 27,3	—	In = 113	—	Tl = 204	—
	C = 12	Si = 28	—	Sn = 118	—	Pb = 207	—
	N = 14	P = 31	As = 75	Sb = 122	—	Bi = 208	—
	O = 16	S = 32	Se = 78	Te = 125?	—	—	—
	F = 19	Cl = 35,5	Br = 80	J = 127	—	—	—



Высшій оксидъ, образующій соли:	Группа I. R^2O	Группа II. R^2O^3 или RO	Группа III. R^2O^3	Группа IV. R^2O^4 или RO^2	Группа V. R^2O^5	Группа VI. R^2O^6 или RO^3	Группа VII. R^2O^7	Группа VIII (переходъ къ I). R^2O^8 или RO^4
Рядъ 1	H=1			RH^4	RH^3	RH^2	RH	
Рядъ 2 (typical)	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
Рядъ 3	Na=23	Mg=24	Al=27,5	Si=28	P=31	S=32	Cl=35,5	
Рядъ 4	K=39	Ca=40	———	Ti=48(?)	V=51	Cr=52	Mn=55	Fe=56	Co=59	Ni=59	Cu=63
Рядъ 5	Cu=63	Zn=65	———	———	As=75	Se=78	Br=80				
Рядъ 6	Rb=85	Sr=87	Yt=88?	Zr=90	Nb=94	Mo=96	———	Ru=104	Rh=104	Pd=106	Ag=108
Рядъ 7	Ag=108	Cd=112	In=113	Sn=118	Sb=122	Te=125(?)	J=127				
Рядъ 8	Cs=133	Ba=137	Di=138?	Ce=140(?)	149	146	149	150	151	152	153
Рядъ 9	———	———	———	———	———	———	———				
	153	156	160	162	164	166	196				
Рядъ 10	———	———	Er=178?	La=180?	Ta=182	W=184	———	Os=193	Ir=195	Pt=197	Au=197
	175	177					190				
Рядъ 11	Au=197	Hg=200	Tl=204	Pb=207	Bi=208	———	———				
						210	212				
Рядъ 12	———	———	———	Th=231	———	U=240	———	———	———	———	———
	220	225	227		235		245	246	248	249	250

(Фотовоспроизведение таблицы-наклейки «Основы химии», изд. 2, СПб., 1873, в начале тома)

Table 39 (p 15)

	Первая группа	Вторая группа	Третья группа	Четвертая группа	Пятая группа	Шестая группа	Седьмая группа	Восьмая группа
Ряды	» R^2O	» RO	» R^2O^3	RH^4 RO^2	RH^3 R^2O^5	RH^2 RO^3	RH R^2O^7	(R^2H) (RO^4)
1. .	1 H							
2. .	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
3. .	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35 Cl	
4. .	K 39	Ca 40	?44	Ti 48	V 51	Cr 52	Mn 55	Fe 56, Co 59, Ni 59, Cu 63
5. .	(63 Cu)	65 Zn	68?	72 ?	75 As	78 Se	80 Br	
6. .	Rb 85	Sr 87	Yt 88	Zr 90	Nb 94	Mo 96	? 100	Ru 104, Rh 104, Pl 106, Ag 108
7. .	(108 Ag)	112 Cd	113 In	118 Sn	122 Sb	125 Te	127 J	
8. .	Cs 133	Ba 137	?DI 138	Ce 140	»	»	»	» » » »
9. .	»	»	»	»	»	»	»	
10. .	»	»	Er 178	?La 180	Ta 182	W 184	? 190	Os 195, Ir 197, Pt 198, Au 199
11. .	(199 Au)	200 Hg	204 Tl	207 Pb	208 Bi	»	»	
12. .	»	»	»	Th 231	»	U 240	»	» » » »

Table 40 (14)

	I	II	III	IV	V	VI	VII	VIII
1	1H							
2	Li7	Be9.4	B11	C12	N14	O16	F19.	
3	23Na	24Mg	27Al	28Si	31P	32S	35.5Cl	
4	K39	Ca40	44	Ti48	V51	Cr52	Mn55	Fe56, Co59, Ni59, Cu63
5	[63Cu]	65Zn	68Ga	72	75As	78Se	80Br	
6	Rb85	Sr87	Yt89	Zr90	Nb94	Mo96	-	Ru104, Rh104, Pl106, Ag108
7	[108Ag]	112Cd	113In	118Sn	122Sb	125Te	127I	
8	Cs133	Ba137	Di,La	Ce138	-	-	-	- - - -
9	-	-	-	-	-	-	-	
10	-	-	Er171	La,Di	Ta182	W184	-	Os195, Ir197, Pt198, Au199
11	[199Au]	200Hg	204Tl	207Pb	208Bi	-	-	
12	-	-	-	Th231	-	U240	-	- - - -

Table 4 (p. 16)

[XII] ПЕРИОДИЧЕСКАЯ СИСТЕМА ХИМИЧЕСКИХ ЭЛЕМЕНТОВ, ОСНОВАННАЯ НА ИХ АТОМНОМ ВЕСЕ И ХИМИЧЕСКОМ СХОДСТВЕ

Группы	I	II	III	IV	V	VI	VII	VIII
Ряды	R^2O	RO	R^2O^3	RH^4 RO^2	RH^3 R^2O^5	RH^2 RO^3	RH R^2O^7	(R^2H) Водородные соединения (RO^4) Высшее кислородное соединение
1.	1 H	—	—	—	—	—	—	
2.	Li 7	Be 9,4	B 11	C 12	N 14	O 16	F 19	
3.	23 Na	24 Mg	27,3 Al	28 Si	31 P	32 S	35,5 Cl	
4.	K 39	Ca 40	? 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56, Co 59, Ni 59, Cu 63
5.	(63 Cu)	65 Zn	68 Ga	72 ?	75 As	78 Se	80 Br	
6.	Rb 85	Sr 87	Yt 88	Zr 90	Nb 94	Mo 96	? 100	Ru 104, Rh 104, Pl 106, Ag 108
7.	(108 Ag)	112 Cd	113 In	118 Sn	122 Sb	125 Te	127 J	
8.	Cs 133	Ba 137	La? 138	Ce 139	Di? 142 ?	—	—	
9.	—	—	—	—	—	—	—	
10.	—	—	Er 175	? 180	Ta 182	W 184	? 190	Os 193, Ir 195, Pt 197, Au 197
11.	(197 Au)	200 Hg	204 Tl	207 Pb	208 Bi	—	—	
12.	—	—	—	Th 234	? 237	U 240	—	

Table 42 (p. 17)

											{ типические элементы }							
											H	Li	Be	B	C	N	O	F
												Na	Mg	Al	Si	P	S	Cl
Четные ряды																		
K	Ca	?	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	..	Zn	Ga	?	As	Se	Br	
Rb	Sr	Y	Zr	Nb	Mo	?	Ru	Rh	Pd	Ag	..	Cd	In	Sn	Sb	Te	J	
Cs	Ba	La	Ce	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	Er	?	Ta	W	?	Os	Ir	Pt	Au	..	Hg	Tl	Pb	Bi	—	—	
—	—	—	Th	?	U						Нечетные ряды							

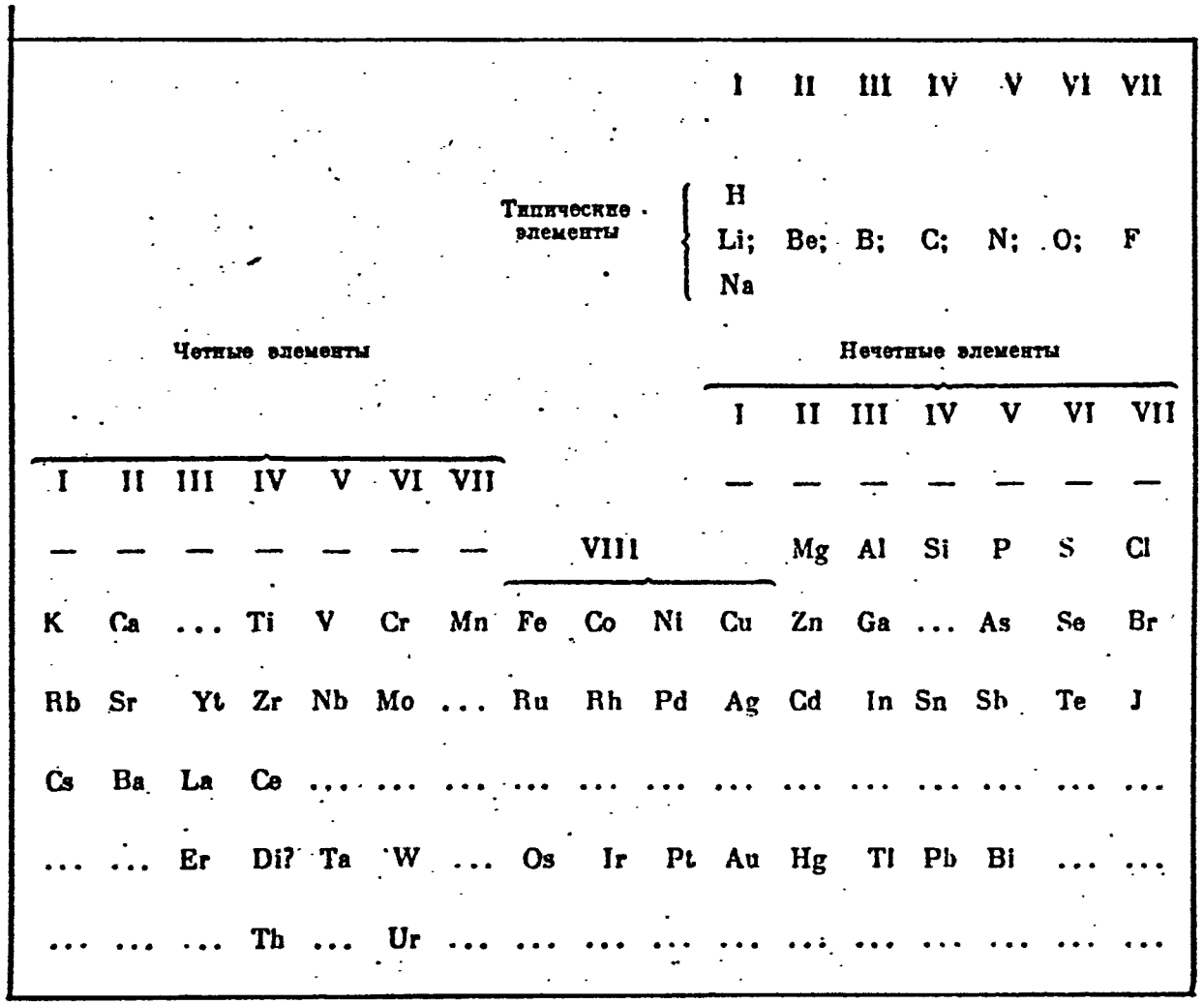
[1432] ПЕРИОДИЧЕСКАЯ СИСТЕМА ЭЛЕМЕНТОВ

II . . . . Li; Be; B; C; N; O; F. Типичные элементы.

I	II	III	IV	V	VI	VII	VIII			I	II	III	IV	V	VI	VII
							———			Na	Mg	Al	Si	P	S	Cl
K	Ca	—	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—	As	Se	Br
Rb	Sr	Yt	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J
Cs	Ba	La	Ce	?	—	—	—	—	—	—	—	—	—	—	—	—
—	—	Er	Di?	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	--	--
—	—	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	--

Table43(P18)

Table 44 (p. 9)



										I	II	III	IV	V	VI	VII
							Типические элементы			H						
										Li;	Be;	B;	C;	N;	O;	F
										Na						
			Четные элементы									Нечетные элементы				
										I	II	III	IV	V	VI	VII
I	II	III	IV	V	VI	VII				—	—	—	—	—	—	—
—	—	—	—	—	—	—		VIII			Mg	Al	Si	P	S	Cl
K	Ca	...	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	...	As	Se	Br
Rb	Sr		Yt	Zr	Nb	Mo	...	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J
Cs	Ba		La	Ce	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...		Er	Di?	Ta	W	...	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	...	...
...	...		...	Th	...	Ur	...	...	...	...	...	...	...	...	...	...	...

Gruppen	Reihen: 1	2	4	6	8	10	12
I.		Li = 7	K (39)	Rb (85)	Cs (133)	—	—
II.		Be = 9.2	Ca (40)	Sr (87)	Ba (137)	—	—
III.		B = 11	? Sc [1])	Yt (89 ?)	? Di (139 ?)	Er (175 ?)	—
IV.		C = 12	Ti (48)	Zr (90)	Ce (141)	? La (180 ?)	Th (231)
V.		N = 14	V (51)	Nb (94)	(? [2])	Ta (182)	—
VI.		O = 16	Cr (52.5)	Mo (96)	?	W (184)	Ur (240)
VII.		F = 19	Mn (55)	—	—	—	—
			Fe (56)	Ru (103)	—	Os (194 ?)	—
VIII.			Co (58.6)	Rh (104)	—	Jr (195 ?)	—
			Ni (58.6)	Pd (106)	—	Pt (197)	—
I.	H = 1	Na = 23	Cu (63.5)	Ag (108)	—	Au (197)	—
II.		Mg (24)	Zn (65)	Cd (112)	[3])	Hg (200)	—
III.		Al (27.3)	Ga (69)	Jn (113)	—	Tl (204)	—
IV.		Si (28)	? ? ?	Sn (118)	—	Pb (204)	—
V.		P (31)	As (75)	Sb (120) [4])	—	Bi (208)	—
VI.		S (32)	Se (79)	Te (125 ?)	—	—	—
VII.		Cl (35.5)	Br (80)	Jod (127)	—	—	—
	Reihen	3	5	7	9	11	

Typische Elemente

St. Petersburg, 4./16. April 1880.

[1]) Wie bekannt, beansprucht Hr. Cleve diesen Ort für das von ihm untersuchte Scandium.
[2]) Diesen Ort würde möglicherweise Didym (Di = 146) einnehmen, wenn seine Oxyde der Formel DiO_2, seine Superoxyde Di_2O_5 entsprechen.
[3]) An diesen Ort stellt Hr. Carnelley (Philos. Magas. 1879, pg. 312, Oct.) das durch Hrn. Dahll entdeckte Norwegium, Ng = 146.
[4]) Cooke Proceedings of the american Academie (March 1880) p. 251

[XV] ПЕРИОДИЧЕСКАЯ СИСТЕМА ХИМИЧЕСКИХ ЭЛЕМЕНТОВ

РАСПОЛОЖЕНИЕ ЭЛЕМЕНТОВ ПО ГРУППАМ И РЯДАМ.

Группа:	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Ряд 1.	. H			RH^4	RH^3	RH^2	RH	Водородные соедин.
— 2.	Li .	Be .	B .	C .	N .	O .	F .	
— 3.	. Na	. Mg	. Al	. Si	. P	.. S	. Cl	
— 4.	K .	Ca ..	Sc .	Ti .	V .	Cr .	Mn .	Fe. Co. Ni. Cu.
— 5.	. (Cu)	. Zn	. Ga	. ?	. As	. Se	. Br	
— 6.	Rb .	Sr .	Y .	Zr .	Nb .	Mo .	— .	Ru. Rh. Pd. Ag.
— 7.	. (Ag)	. Cd	. In	. Sn	. Sb	. Te	. J	
— 8.	Cs .	Ba .	La .	Ce .	Di .	— .	— .	— — — —
— 9.	. —	. —	. —	. —	. —	. —	. —	
— 10.	— .	— .	Yb .	— .	Ta .	W .	— .	Os. Ir. Pt. Au.
— 11.	. (Au)	. Hg	. Tl	. Pb	. Bi	. —	. —	
— 12.	— .	— .	— .	Th .	— .	U .	— .	
	R^2O	R^2O^2 RO	R^2O^3	R^2O^4 RO^2	R^2O^5	R^2O^6 RO^3	R^2O^7	Высшие окислы. RO^4

Table46(T21)

[XVI] ПЕРИОДИЧЕСКАЯ СИСТЕМА ХИМИЧЕСКИХ ЭЛЕМЕНТОВ, ОСНОВАННАЯ НА ИХ АТОМНОМ ВЕСЕ, ВЫРАЖАЮЩАЯ ИХ СХОДСТВО И СООТВЕТСТВУЮЩАЯ ИХ СПОСОБНОСТИ К СОЕДИНЕНИЮ С КИСЛОРОДОМ, ВОДОРОДОМ И ДР. ЭЛЕМЕНТАМИ

Расположение элементов по периодам.

R^2O	I		Li = 7	K 39	Rb 85	Cs 133	— —	— —
RO	II		Be = 9	Ca 40	Sr 87	Ba 137	— —	— —
R^2O^3	III		B = 11	Sc 44	Y 89	La 138	Yb 173	— —
RO^2	IV	(H^4C)	C = 12	Ti 48	Zr 90	Ce 142	— —	Th 231
R^2O^5	V	(H^3N)	N = 14	V 51	Nb 94	Di 146	Ta 182	— —
RO^3	VI	(H^2O)	O = 16	Cr 52	Mo 96	— —	W 184	U 240
R^2O^7	VII	(HF)	F = 19	Mn 55	— —	— —	— —	— —
RO^4				Fe 56	Ru 103	— —	Os 192?	— —
	VIII			Co 58	Rh 104	— —	Ir 193	— —
				Ni 59	Pd 106	— —	Pt 195	— —
R^2O	I	H = 1	Na = 23	Cu 63	Ag 108	— —	Au 196	— —
RO	II		Mg 24	Zn 65	Cd 112	— —	Hg 200	— —
R^2O^3	III		Al 27	Ga 69	In 113	— —	Tl 204	— —
RO^2	IV	(H^4R)	Si 28	?? 72	Sn 118	— —	Pb 206	— —
R^2O^5	V	(H^3R)	P 31	As 75	Sb 120	— —	Bi 209	— —
RO^3	VI	(H^2R)	S 32	Se 79	Te 125?	— —	— —	— —
R^2O^7	VII	(HR)	Cl 35,5	Br 80	J 127	— —	— —	— —
Период:			1-й	2-й	3-й	4-й	5-й	6-й

Двойною чертою отделены: типические элементы.

Table47(P22)

Table48(P23)

											(типические элементы)						
											H	Li	Be	B	C	N	O	F	Na
												Na	Mg	Al	Si	P	S	Cl	
Четные ряды																			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	..	Zn	Ga	?	As	Se	Br		
Rb	Sr	Y	Zr	Nb	Mo	?	Ru	Rh	Pd	Ag	..	Cd	In	Sn	Sb	Te	J		
Cs	Ba	La	Ce	Di	—	—	—	—	—	—	—	—	—	—	—	—	—		
—	—	Yb	?	Ta	W	?	Os	Ir	Pt	Au	..	Hg	Tl	Pb	Bi	—	—		
—	—	—	Th	?	U							Нечетные ряды							

Table 49(15)

Группа	I	II	III	IV	V	VI	VII	VIII
					RH^3	RH^2	RH	Водородные соединения
Ряд 1	H_1			RH^4				
» 2	Li_7	Be_9	B_{11}	C_{12}	N_{14}	O_{16}	F_{19}	
» 3	Na_{23}	Mg_{24}	Al_{27}	Si_{28}	P_{31}	S_{32}	$Cl_{35,5}$	
» 4	K_{39}	Ca_{40}	Sc_{44}	Ti_{48}	U_{51}	Cr_{52}	Mn_{55}	$Fe_{56}Co_{58}Ni_{59}Cu_{63}$
» 5	(Cu_{63})	Zn_{65}	Ga_{69}	Ge_{72}	As_{75}	Se_{79}	Br_{80}	
» 6	Rb_{85}	Sr_{87}	Y_{89}	Zr_{90}	Nb_{94}	Mo_{96}	—	$Ru_{103}Rh_{104}Pd_{106}Ag_{108}$
» 7	(Ag)	Cd_{112}	In_{113}	Sn_{118}	Sb_{120}	Te_{125}	J_{127}	
» 8	Cs_{133}	Ba_{137}	La_{138}	Ce_{142}	Di_{146}	—	—	— —
» 9	—	—	—	—	—	—	—	
» 10	—	—	Yb_{173}	—	Ta_{182}	W_{184}	—	$Os_{192}Ir_{193}Pt_{195}Au_{196}$
» 11	(Au)	Hg_{200}	Tl_{204}	Pb_{206}	Bi_{209}	—	—	
» 12	—	—	—	Th_{231}	—	U_{240}	—	
	R^2O	R^2O^2 RO	R^2O^3	R^2O^4 RO^2	R^2O^5	R^2O^6 RO^3	R^2O^7	Высшие окислы RO^4

РАСПОЛОЖЕНИЕ ЭЛЕМЕНТОВ ПО ПЕРИОДАМ

R^2O	I	Li = 7	K = 39	Rb = 85	Cs = 133	—	—	—	—	—	—	—	—
RO	II	Be = 9	Ca = 40	Sr = 87	Ba = 137	—	—	—	—	—	—	—	—
R^2O^3	III	B = 11	Sc = 44	Y = 89	La = 138	Yb = 173	—	—	—	—	—	—	—
RO^2	IV (H^4C)	C = 12	Ti = 48	Zr = 90	Ce = 142	—	—	Th = 231					
R^2O^5	V (H^3N)	N = 14	V = 51	Nb = 94	Di = 146	Ta = 182	—	—					
RO^3	VI (H^2O)	O = 16	Cr = 52	Mo = 96	—	—	W = 184	U = 240					
R^2O^7	VII (HF)	F = 19	Mn = 55	—	—	—	—	—	—	—	—	—	—
RO^4			Fe = 56	Ru = 103	—	—	Os = 192?	—	—	—	—	—	—
	VIII		Co = 58	Rh = 104	—	—	Ir = 193	—	—	—	—	—	—
			Ni = 59	Pd = 106	—	—	Pt = 195	—	—	—	—	—	—
R^2O	I H = 1	Na = 23	Cu = 63	Ag = 108	—	—	Au = 196	—	—	—	—	—	—
RO	II	Mg = 24	Zn = 65	Cd = 112	—	—	Hg = 200	—	—	—	—	—	—
R^2O^3	III	Al = 27	Ga = 69	In = 113	—	—	Tl = 204	—	—	—	—	—	—
RO^2	IV (H^4R)	Si = 28	Ge = 72	Sn = 118	—	—	Pb = 206	—	—	—	—	—	—
R^2O^5	V (H^3R)	P = 31	As = 75	Sb = 129	—	—	Bi = 209	—	—	—	—	—	—
RO^3	VI (H^2R)	S = 32	Se = 79	Te = 125	—	—	—	—	—	—	—	—	—
R^2O^7	VII (HR)	Cl = 35	Br = 80	J = 127	—	—	—	—	—	—	—	—	—
Период		1-й	2-й	3-й	4-й	5-й	6-й						

Table50(L6)

Группа:	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Ряд 1.	. H			RH^4 .	RH^3 .	RH^2 .	RH .	Водородные соедин.
» 2.	Li .	Be .	B .	C .	N .	O .	F .	
» 3.	. Na	. Mg	. Al	. Si	. P	. S	. Cl	
» 4.	K .	Ca .	Sc .	Ti .	V .	Cr .	Mn .	Fe. Co. Ni. Cu.
» 5.	. (Cu)	. Zn	. Ga	. Ge	. As	. Se	. Br	
» 6.	Rb .	Sr .	Y .	Zr .	Nb .	Mo .	— .	Ru. Rh. Pd. Ag.
» 7.	. (Ag)	. Cd	. In	. Sn	. Sb	. Te	. J	
» 8.	Cs .	Ba .	La .	Ce .	Di? .	— .	— .	— — — —
» 9.	. —	. —	. —	. —	. —	. —	. —	
» 10.	— .	— .	Yb .	— .	Ta .	W .	— .	Os. Ir. Pt. Au.
» 11.	. (Au)	. Hg	. Tl	. Pb	. Bi	. —	. —	
» 12.	— .	— .	— .	Th .	— .	U .	— .	
	R^2O	R^2O^2 RO	R^2O^3	R^2O^4 RO^2	R^2O^5	R^2O^6 RO^3	R^2O^7	Высшие окислы. RO^4

(VIII) АТОМНЫЕ ВЕСА ЭЛЕМЕНТОВ

РАСПРЕДЕЛЕНИЕ ЭЛЕМЕНТОВ ПО ПЕРИОДАМ

Группы	Высшие солеобразные окислы	Типический или 1-й малый период	Большие периоды: 1-й	2-й	3-й	4-й	5-й
I	R^2O	Li = 7	K 39	Rb 85	Cs 133	— —	— —
II	RO	Be = 9	Ca 40	Sr 87	Ba 137	— —	— —
III	R^2O^3	B = 11	Sc 44	Y 89	La 138	Yb 173	— —
IV	RO^2	C = 12	Ti 48	Zr 90	Ce 140	— —	Th 232
V	R^2O^5	N = 14	V 51	Nb 94	— —	Ta 182	— —
VI	RO^3	O = 16	Cr 52	Mo 96	— —	W 184	Ur 240
VII	R^2O^7	F = 19	Mn 55	— —	— —	— —	— —
VIII			Fe 56	Ru 103	— —	Os 191	— —
			Co 58½	Rh 104	— —	Ir 193	— —
			Ni 59	Pd 106	— —	Pt 196	— —
I	R^2O	H = 1 Na = 23	Cu 63	Ag 108	— —	Au 198	— —
II	RO	Mg = 24	Zn 65	Cd 112	— —	Hg 200	— —
III	R^2O^3	Al = 27	Ga 70	In 112	— —	Tl 204	— —
IV	RO^2	Si = 28	Ge 72	Sn 118	— —	Pb 206	— —
V	R^2O^5	P = 31	As 75	Sb 120	— —	Bi 208	— —
VI	RO^3	S = 32	So 79	Te 125	— —	— —	— —
VII	R^2O^7	Cl = 35½	Br 80	J 127	— —	— —	— —
		2-й малый период.	1-й	2-й	3-й	4-й	5-й
			Большие периоды.				

Table52(P25)

Table 53 (p. 26)

										(типические элементы)						
										H						
										Li	Be	B	C	N	O	F
										Na	Mg...					
											Mg	Al	Si	P	S	Cl
				Четные ряды												
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J
Cs	Ba	La	Ce	Di?	—	—	—	—	—	—	—	—	—	—	—	—
—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
—	—	—	Th	—	U											
													Нечетные ряды			

[X] РАСПОЛОЖЕНИЕ ЭЛЕМЕНТОВ ПО ГРУППАМ И РЯДАМ

ГРУППЫ:	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Ряд 1.	. H							
» 2.	Li .	Be .	B .	C .	N .	O .	F .	
» 3.	. Na	. Mg	. Al	. Si	. P	. S	. Cl	
» 4.	K .	Ca .	Sc .	Ti .	V .	Cr .	Mn .	Fe. Co. Ni. Cu.
» 5.	. (Cu)	. Zn	. Ga	. Ge	. As	. Se	. Br	
» 6.	Rb .	Sr .	Y .	Zr .	Nb .	Mo .	— .	Ru. Rh. Pd. Ag.
» 7.	. (Ag)	. Cd	. In	. Sn	. Sb	. Te	. J	
» 8.	Cs .	Ba .	La .	Ce .	Di? .	— .	— .	— — — —
» 9.	. —	. —	. —	. —	. —	. —	. —	
» 10.	— .	— .	Yb .	— .	Ta .	W .	— .	Os. Ir. Pt. Au.
» 11.	. (Au)	. Hg	. Tl	. Pb	. Bi	. —	. —	
» 12.	— .	— .	— .	Th .	— .	U .	— .	
	R^2O	R^2O^2 . RO	R^2O^3	R^2O^4 RO^2	R^2O^5	R^2O^6 RO^3	R^2O^7	Высшие окислы. RO^4
	—	—	—	. RH^4	. RH^3	. RH^2	. RH	Водородные соед.

table54(p27)

(XI) ПЕРИОДИЧЕСКАЯ СИСТЕМА И АТОМНЫЕ ВЕСА ЭЛЕМЕНТОВ

(с указанием страниц, на которых они описаны)

	2-й ряд. Типические элементы.	4-й ряд:	6-й ряд:	8-й ряд:	10-й ряд:	12-й ряд:
I	Li 7 стр. 398.	K 39 стр. 377.	Rb 86 стр. 400.	Cs 133 стр. 400.	—	—
II	Be 9 стр. 427.	Ca 40 стр. 409.	Sr 88 стр. 425.	Ba 137 стр. 425.	—	—
III	B 11 стр. 473.	Sc 44 стр. 496.	Y 89 стр. 496.	La 138 стр. 496.	Yb 173 стр. 496.	—
IV	C 12 стр. 238.	Ti 48 стр. 533.	Zr 91 стр. 534.	Ce 140 стр. 496.	? 178	Th 232 стр. 535.
V	N 14 стр. 159.	V 51 стр. 568.	Nb 94 стр. 569.	?Di 142 стр. 496.	Ta 183 стр. 569.	—
VI	O 16 стр. 109.	Cr 52 стр. 623.	Mo 96 стр. 633.	—	W 184 стр. 633.	U 239 стр. 639.
VII	F 19 стр. 341.	Mn 55 стр. 642.	? 99	—	—	—
VIII		Fe 56 стр. 651.	Ru 102 стр. 691.	—	Os 192 стр. 691.	
		Co 59 стр. 677.	Rh 103 стр. 691.	—	Ir 193 стр. 697.	
		Ni 59,5 стр. 677.	Pd 106 стр. 691.	—	Pt 196 стр. 691	

	3-й ряд:	5-й ряд:	7-й ряд:	9-й ряд:	11-й ряд:
I H 1 стр. 82.	Na 23 стр. 356.	Cu 64 стр. 711.	Ag 108 стр. 723.	—	Au 197 стр. 743.
II	Mg 24 стр. 409.	Zn 65 стр. 458.	Cd 112 стр. 463.	—	Hg 200 стр. 464.
III	Al 27 стр. 479.	Ga 70 стр. 94.	In 114 стр. 494.	—	Tl 204 стр. 495.
IV	Si 28 стр. 499.	Ge 72 стр. 519.	Sn 119 стр. 519.	—	Pb 207 стр. 525.
V	P 31 стр. 536.	As 75 стр. 556.	Sb 120 стр. 562.	—	Bi 209 стр. 565.
VI	S 32 стр. 571.	So 79 стр. 619.	Te 125 стр. 621.	—	—
VII	Cl 35,5 стр. 294.	Br 80 стр. 344.	J 127 стр. 346.	—	—

(Двумя чертами означены те из элементов, которые весьма распространены в природе. Одною подчеркнуты те, которые, хотя и не часто встречаются в природе, но имеют значительное распространение в промышленности и обиходе).

Группы.						
I	Li	K	Rb	Cs	—	—
II	Be	Ca	Sr	Ba	—	—
III	B	Sc	Y	La	Yb	—
IV	C	Ti	Zr	Ce	—	Th
V	N	V	Nb	Di?	Ta	—
VI	O	Cr	Mo	—	W	U
VII	F	Mn	—	—	—	—
VIII	—	Fe	Ru	—	Os	—
	—	Co	Rh	—	Ir	—
	—	Ni	Pd	—	Pt	—
I . . .	HNa	Cu	Ag	—	Au	—
II	Mg	Zn	Cd	—	Hg	—
III	Al	Ga	In	—	Tl	—
IV	Si	Ge	Sn	—	Pb	—
V	P	As	Sb	—	Bi	—
VI	S	Se	Te	—	—	—
VII	Cl	Br	J	—	—	—

Table56(P29)

ПЕРИОДЫ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ, СЧИТАЯ АТОМНЫЙ ВЕС КИСЛОРОДА O = 16©

Газообр. водородные соед.	Высшие солеобр. окислы	Группы	Типические элементы		Высшие солеобразн. окислы	Группы	Элементы четных рядов				
					R^2O	I	K = 39,1	Rb = 85,4	Cs = 132,9	—	—
					RO	II	Ca = 40,1	Sr = 87,6	Ba = 137,4	—	Rd = 224 *******
					R^2O^3	III	Sc = 44,1	Y = 89,0	La = 139	Yb = 173	—
					RO^2	IV	Ti = 48,1	Zr = 90,6	Ce = 140 ******	—	Th = 232
					R^2O^5	V	V = 51,4	Nb = 94,0	—	Ta = 183	—
					RO^3	VI	Cr = 52,1	Mo = 96,0	—	W = 184	U = 239
					R^2O^7	VII	Mn = 55,0	? = 99 ****	—	—	
						VIII	Fe = 55,9	Ru = 101,7	—	Os = 191	
							Co = 59	Rh = 103,0	—	Ir = 193	
							Ni = 59 ***	Pd = 106,5	—	Pt = 194,9	
	R^2O	I	H = 1,008	Li = 7,03	Na = 23,05		Cu = 63,6	Ag = 107,9	—	Au = 197,2	
	RO	II		Be = 9,1	Mg = 24,3		Zn = 65,4	Cd = 112,4	—	Hg = 200,0	
	R^2O^3	III		B = 11,0	Al = 27,0		Ga = 70,0	In = 114,0	—	Tl = 204,1	
RH^4	RO^2	IV		C = 12,0	Si = 28,4		Ge = 72,3	Sn = 119,0	—	Pb = 206,9	
RH^3	R^2O^5	V		N = 14,04	P = 31,0		As = 75,0	Sb = 120,0	—	Bi = 208,5	
RH^2	RO^3	VI		O = 16,00	S = 32,06		Se = 79	Te = 127 *****	—	—	
RH	R^2O^7	VII		F = 19,0	Cl = 35,45		Br = 79,95	J = 127	—	—	
0	0	0 *	He = 4,0	Ne = 19,9	Ar = 38**		K = 81,8	Xe = 128	—	—	

Элементы нечетных рядов

Д. Менделеев
1869—1902

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* Для гелия, аргона и аналогических им газов, судя по их плотности (стр. 179—183), вес атома более, чем для галоидов, и менее, чем для щелочных металлов, а соединений неизвестно.

** Плотность аргона указывает на вес атома 39,9, но, суди по тому, что сказано в предшествующей выноске, должно думать, что атомный вес Ar более, чем Cl, но менее, чем K, т. е. около 38.

*** Для Ni находится атомный вес 58,7, но так как этот металл, судя по свойствам, должен следовать за Co = 59, то у него должно ждать атомного веса не меньшего, а большего, чем для Co, а потому для Co и Ni при дальнейшем исследовании можно ждать некоторого (небольшого) изменения величины атомного веса.

**** Можно ждать открытия металла, сходного с Mn (экамарганец), с атомным весом около 99.

***** Судя по свойствам и по периодической системе, теллур должен иметь атомный вес меньший, чем под, а опыт дает доныне обратное: для теллура от 126,4 (Штейнер) до 127,9 (Метцнер), в среднем 127,7, а для пода немного менее, а именно по Стасу 126,96, а по Ладенбургу 126,98. Оба числа близки к 127, а потому можно полагать, что либо атомный вес пода при дальнейшем исследовании окажется более 127 (это возможно, т. к. под сушили $CaCl^2$, а это может вводить хлор), или для теллура получится число менее 127.

****** Между Ce = 140 и Ta = 183 недостает целого большого периода, но ряд редких элементов (изучение их не полно), например Pr = 140,5, Nd = 143,6, Gd = 156, Er = 166, Yb = 173 и др., представляет, по современным сведениям, вес атома, как раз восполняющий этот промежуток, а потому в указанном месте периодическая система элементов представляет своего рода разрыв, требующий новых изысканий.

******* По исследованиям г-жи Кюри (1902) *радий* (стр. 675) (один из радиоактивных элементов) сходен с барием и имеет атомный вес от 223 до 225.

Періодическая система элементовъ, по группамъ и рядамъ.

Ряды.	ГРУППЫ ЭЛЕМЕНТОВЪ: 0	I	II	III	IV	V	VI	VII	VIII
1	—	Водородъ. H 1,008	—	—	—	—	—	—	
2	Гелій. He 4,0	Литій. Li 7,03	Берилій. Be 9,1	Боръ. B 11,0	Углеродъ. C 12,0	Азотъ. N 14,04	Кислородъ. O 16,00	Фторъ F 19,0	
3	Неонъ. Ne 19,9	Натрій. Na 23,05	Магній. Mg 24,3	Алюминій. Al 27,0	Кремній. Si 28,4	Фосфоръ. P 31,0	Сѣра. S 32,06	Хлоръ. Cl 35,45	
4	Аргонъ. Ar 38	Калій. K 39,1	Кальцій. Ca 40,1	Скандій. Sc 44,1	Титанъ. Ti 48,1	Ванадій. V 51,4	Хромъ. Cr 52,1	Марганецъ. Mn 55,0	Желѣзо. Fe 55,9 / Кобальтъ. Co 59 / Никкель. Ni 59 (Cu)
5		Мѣдь. Cu 63,6	Цинкъ. Zn 65,4	Галлій. Ga 70,0	Германій. Ge 72,3	Мышьякъ. As 75	Селенъ. Se 79	Бромъ. Br 79,95	
6	Криптонъ. Kr 81,8	Рубидій. Rb 85,4	Стронцій. Sr 87,6	Иттрій. Y 89,0	Цирконій. Zr 90,6	Ніобій. Nb 94,0	Молибденъ. Mo 96,0	—	Рутеній. Ru 101,7 / Родій. Rh 103,0 / Палладій. Pd 106,5 (Ag)
7		Серебро. Ag 107,9	Кадмій. Cd 112,4	Индій. In 114,0	Олово. Sn 119,0	Сурьма. Sb 120,0	Теллуръ. Te 127	Іодъ. J 127	
8	Ксенонъ. Xe 128	Цезій. Cs 132,9	Барій. Ba 137,4	Лантанъ. La 139	Церій. Ce 140	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Иттербій. Yb 173	—	Танталъ. Ta 183	Вольфрамъ. W 184	—	Осмій. Os 191 / Иридій. Jr 193 / Платина. Pt 194,9 (Au)
11		Золото. Au 197,2	Ртуть. Hg 200,0	Талій. Tl 204,1	Свинецъ. Pb 206,9	Висмутъ. Bi 208	—	—	
12	—	—	Радій. Rd 224	—	Торій. Th 232	—	Уранъ. U 239		
Высшіе солеобразные окислы:	R	R^2O	RO	R^2O^3	RO^2	R^2O^5	RO^3	R^2O^7	RO^4
Высшія газообразныя водородныя соединенія:					RH^4	RH^3	RH^2	RH	

(Фотовоспроизведение таблицы. «Основы химии», изд. 7, СПб., 1903, стр. X)

Table59(p32)

										(типические элементы)						
										H						
										Li	Be	B	C	N	O	F
										Na	Mg...					
I	II	III	IV	V	VI	VII		VIII		I	II	III	IV	V	VI	VII
Четные ряды																
											Mg	Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J
Cs	Ba	La	Ce	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
—	—	—	Th	—	U											
											Нечетные ряды					

Table60(P33)

Series	Zero Group	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII			
0	x											
1		Hydrogen H=1·008										
2	Helium He=4·0	Lithium Li=7·03	Beryllium Be=9·1	Boron B=11·0	Carbon C=12·0	Nitrogen N=14·04	Oxygen O=16·00	Fluorine F=19·0				
3	Neon Ne=19·9	Sodium Na=23·05	Magnesium Mg=24·1	Aluminium Al=27·0	Silicon Si=28·4	Phosphorus P=31·0	Sulphur S=32·06	Chlorine Cl=35·45				
4	Argon Ar=38	Potassium K=39·1	Calcium Ca=40·1	Scandium Sc=44·1	Titanium Ti=48·1	Vanadium V=51·4	Chromium Cr=52·1	Manganese Mn=55·0	Iron Fe=55·9	Cobalt Co=59	Nickel Ni=59	(Cu)
5		Copper Cu=63·6	Zinc Zn=65·4	Gallium Ga=70·0	Germanium Ge=72·3	Arsenic As=75·0	Selenium Se=79	Bromine Br=79·95				
6	Krypton Kr=81·8	Rubidium Rb=85·4	Strontium Sr=87·6	Yttrium Y=89·0	Zirconium Zr=90·6	Niobium Nb=94·0	Molybdenum Mo=96·0	—	Ruthenium Ru=101·7	Rhodium Rh=103·0	Palladium Pd=106·5	(Ag)
7		Silver Ag=107·9	Cadmium Cd=112·4	Indium In=114·0	Tin Sn=119·0	Antimony Sb=120·0	Tellurium Te=127	Iodine I=127				
8	Xenon Xe=128	Cæsium Cs=132·9	Barium Ba=137·4	Lanthanum La=139	Cerium Ce=140	—	—		—	—	—	(—)
9		—	—		—	—	—	—				
10	—	—	—	Ytterbium Yb=173	—	Tantalum Ta=183	Tungsten W=184	—	Osmium Os=191	Iridium Ir=193	Platinum Pt=194·9	(Au)
11		Gold Au=197·2	Mercury Hg=200·0	Thallium Tl=204·1	Lead Pb=206·9	Bismuth Bi=208	—	—				
12	—	—	Radium Rd=224	—	Thorium Th=232	—	Uranium U=239					

Table 61 (p. 34)

Ряды	Группа нулевая	Группа I	Группа II	Группа III	Группа IV	Группа V	Группа VI	Группа VII	Группа VIII
0	x								
1	y	Водород H = 1,008							
2	Гелий He = 4,0	Литий Li = 7,03	Бериллий Be = 9,1	Бор B = 11,0	Углерод C = 12,0	Азот N = 14,04	Кислород O = 16,0	Фтор F = 19,0	
3	Неон Ne = 19,9	Натрий Na = 23,05	Магний Mg = 24,1	Алюминий Al = 27,0	Кремний Si = 28,4	Фосфор P = 31,0	Сера S = 32,06	Хлор Cl = 35,45	
4	Аргон Ar = 38	Калий K = 39,1	Кальций Ca = 40,1	Скандий Sc = 44,1	Титан Ti = 48,1	Ванадий V = 51,4	Хром Cr = 52,1	Марганец Mn = 55,0	Железо Fe = 55,9 Кобальт Co = 59 Никкель Ni = 59 (Cu)
5		Медь Cu = 63,6	Цинк Zn = 65,4	Галлий Ga = 70,0	Германий Ge = 72,3	Мышьяк As = 75,0	Селен Se = 79	Бром Br = 79,95	
6	Криптон Kr = 81,8	Рубидий Rb = 85,4	Стронций Sr = 87,6	Иттрий V = 89,0	Циркон Zr = 90,6	Ниобий Nb = 94,0	Молибден Mo = 96,0	—	Рутений Родий Палладий Ru = 101,7 Rh = 103,0 Pd = 106,5 (Ag)
7		Серебро Ag = 107,9	Кадмий Cd = 112,4	Индий In = 114,0	Олово Sn = 119,0	Сурьма Sb = 120.0	Теллур Te = 127	од J = 127	
8	Ксенон Xe = 128	Цезий Cs = 132,9	Барий Ba = 137,4	Лантан La = 139	Церий Ce = 140	—	—	—	— — — (—)
9		—	—	—	—	—	—	—	
10	—	—	—	Иттербий Yb = 173	—	Тантал Ta = 183	Вольфрам W = 184	—	Осмий Иридий Платина Os = 191 Ir = 193 Pt = 194,9 (Au)
11		Золото Au = 197,2	Ртуть Hg = 200,0	Таллий Tl = 204,1	Свинец Pb = 206,9	Висмут Bi = 208	—	—	
12	—	—	Радий Rd = 224	—	Торий Th = 232	—	Уран U = 239	—	

Періодическая система элементовъ по группамъ и рядамъ.

Ряды.	ГРУППЫ ЭЛЕМЕНТОВЪ:								
	0	I	II	III	IV	V	VI	VII	VIII
0	*x*	—	—	—	—	—	—	—	
1	*y*	Водородъ. **H** 1,008	—	—	—	—	—	—	
2	Гелій. **He** 4,0	Литій. **Li** 7,03	Бериллій. **Be** 9,1	Боръ. **B** 11,0	Углеродъ. **C** 12,0	Азотъ. **N** 14,01	Кислородъ. **O** 16,00	Фторъ. **F** 19,0	
3	Неонъ. **Ne** 19,9	Натрій. **Na** 23,05	Магній. **Mg** 24,36	Алюминій. **Al** 27,1	Кремній. **Si** 28,2	Фосфоръ. **P** 31,0	Сѣра. **S** 32,06	Хлоръ. **Cl** 35,45	
4	Аргонъ. **Ar** 38	Калій. **K** 39,15	Кальцій. **Ca** 40,1	Скандій. **Sc** 44,1	Титанъ. **Ti** 48,1	Ванадій. **V** 51,2	Хромъ. **Cr** 52,1	Марганецъ. **Mn** 55,0	Желѣзо. **Fe** 55,9 — Кобальтъ. **Co** 59 — Никкель. **Ni** 59 — (Cu)
5		Мѣдь. **Cu** 63,6	Цинкъ. **Zn** 65,4	Галлій. **Ga** 70,0	Германій. **Ge** 72,5	Мышьякъ. **As** 75	Селенъ. **Se** 79,2	Бромъ. **Br** 79,95	
6	Криптонъ. **Kr** 81,8	Рубидій. **Rb** 85,5	Стронцій. **Sr** 87,6	Иттрій. **Y** 89,0	Цирконій. **Zr** 90,6	Ніобій. **Nb** 94,0	Молибденъ. **Mo** 96,0	—	Рутеній. **Ru** 101,7 — Родій **Rh** 103,0 — Палладій. **Pd** 106,5 — (Ag)
7		Серебро. **Ag** 107,93	Кадмій. **Cd** 112,4	Индій. **In** 115,0	Олово. **Sn** 119,0	Сурьма. **Sb** 120,2	Теллуръ. **Te** 127	Іодъ. **J** 127	
8	Ксенонъ. **Xe** 128	Цезій. **Cs** 132,9	Барій. **Ba** 137,4	Лантанъ. **La** 138,9	Церій. **Ce** 140,2	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Иттербій. **Yb** 173	—	Танталъ. **Ta** 183	Вольфрамъ. **W** 184	—	Осмій. **Os** 191 — Иридій. **Ir** 193 — Платина. **Pt** 194,8 — (Au)
11		Золото. **Au** 197,2	Ртуть. **Hg** 200,0	Талій. **Tl** 204,1	Свинецъ. **Pb** 206,9	Висмутъ. **Bi** 208,5	—	—	
12	—	—	Радій. **Rd** 225	—	Торій. **Th** 232,5	—	Уранъ. **U** 238,5		

(Фотовоспроизведение таблицы. «Попытка химического понимания мирового эфира», СПб., 1905, стр. 25)

Table 62 (P35)

ПЕРИОДЫ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ И ВЕСА ИХ АТОМОВ, СЧИТАЯ АТОМНЫЙ ВЕС КИСЛОРОДА O = 16

Газообр. водородные соед.	Высшие солеобр. окислы	Группы	Легчайшие типические элементы			Высшие солеобразн. окислы	Группы	Элементы четных рядов				
						RO^4	0	Ar = 38	Kr = 81,8	Xe = 128	—	—
	R^2O	I	H = 1,008	Li = 7,03	Na = 23,05	R^2O	I	K = 39,15	Rb = 85,5	Cs = 132,9	—	—
	RO	II		Be = 9,1	Mg = 24,36	RO	II	Ca = 40,1	Sr = 87,6	Ba = 137,4	—	Rd = 225
	R^2O^3	III		B = 11,0	Al = 27,1	R^2O^3	III	Sc = 44,1	Y = 89,0	La = 138,9	Yb = 173	—
RH^4	RO^2	IV		C = 12,0	Si = 28,2	RO^2	IV	Ti = 48,1	Zr = 90,6	Ce = 140,2 *****	—	Th = 232,5
RH^3	R^2O^5	V		N = 14,01	P = 31,0	R^2O^5	V	V = 51,2	Nb = 94,0	—	Ta = 183	—
RH^2	RO^3	VI		O = 16,00	S = 32,06	RO^3	VI	Cr = 52,1	Mo = 96,0	—	W = 184	U = 238,5
RH	R^2O^7	VII		F = 19,0	Cl = 35,45	R^2O^7	VII	Mn = 55,0	? = 99 ***	—	—	
0	0	0	He = 4,0	Ne = 19,9	Ar = 38 *		VIII	Fe = 55,9	Ru = 101,7	—	Os = 191	
								Co = 59	Rh = 103,0	—	Ir = 193	
								Ni = 59 **	Pd = 106,5	—	Pt = 194,8	
								Cu = 63,6	Ag = 107,9	—	Au = 197,2	
								Zn = 65,4	Cd = 112,4	—	Hg = 200,0	
								Ga = 70,0	In = 115,0	—	Tl = 204,1	
								Ge = 72,5	Sn = 119,0	—	Pb = 206,9	
								As = 75,0	Sb = 120,2	—	Bi = 208,5	
								Se = 79,2	Te = 127	—	—	
								Br = 79,95	J = 127 ****	—	—	
								Kr = 81,8	Xe = 128	—	—	

Элементы нечетных рядов

* Плотность аргона указывает на вес атома 39,9, но, судя по тому, что вес атома аргоновых элементов более, чем для галоидов, а менее, чем для щелочных металлов, должно думать, что атомный вес Ar более, чем Cl, но менее, чем K, т. е. около 38. Элементы нулевой группы в этой таблице помещены не только перед началом периодов, но и после их конца, чтобы ясно показать, что они образуют связь такого же рода, какую составляют элементы VIII-й группы.

** Для Ni находится атомный вес 58,7, но так как этот металл, судя по свойствам, должен следовать за Co = 59, то у него должно ждать атомного веса не меньшего, а бо́льшего, чем для Co, а потому для Co и Ni при дальнейших исследованиях можно ждать некоторого (небольшого) изменения величины атомного веса.

*** Можно ждать открытия металла, сходного с Mn (экамарганец), с атомным весом около 99.

**** Судя по свойствам и по периодической системе, теллур должен иметь атомный вес меньший, чем иод, а опыт дает данные обратное: для теллура от 126,4 (Штейнер) до 127,9 (Метцнер), в среднем 127,7, а для иода немного менее, а именно по Стасу 126,96, а по Ладенбургу 126,98. Оба числа близки к 127, а потому можно полагать, что либо атомный вес иода при дальнейшем исследовании окажется более 127 (это возможно, т. к. иод сушили $CaCl^2$, а это может вводить хлор), или для теллура — получится число менее 127. G. P. Baxter в Америке и P. Köthner und Aener в Германии в 1904 г. дают в среднем J = 126,97.

***** Между Ce = 140 и Ta = 183 недостает целого большого периода, но ряд редких элементов (изучение их не полно), например Pr = 141, Nd = 144, Sm = 150, Eu = 152, Gd = 157, Tb = 160, Ho = 165, Er = 166, Tu = 171 и Yb = 173, представляет, по современным сведениям, вес атома, как раз восполняющий этот промежуток, а потому в указанном месте периодическая система элементов представляет своего рода разрыв, требующий новых изысканий.

Періодическая система элементовъ по группамъ и рядамъ.

Ряды.	ГРУППЫ ЭЛЕМЕНТОВЪ:								
	0	I	II	III	IV	V	VI	VII	VIII
1	—	Водородъ. H 1,008	—	—	—	—	—	—	
2	Гелій. He 4,0	Литій. Li 7,03	Бериллій. Be 9,1	Боръ. B 11,0	Углеродъ. C 12,0	Азотъ. N 14,01	Кислородъ. O 16,00	Фторъ. F 19,0	
3	Неонъ. Ne 19,9	Натрій. Na 23,05	Магній. Mg 24,36	Алюминій. Al 27,1	Кремній. Si 28,2	Фосфоръ. P 31,0	Сѣра S 32,06	Хлоръ Cl 35,45	
4	Аргонъ. Ar 38	Калій. K 39,15	Кальцій. Ca 40,1	Скандій. Sc 44,1	Титанъ. Ti 48,1	Ванадій. V 51,2	Хромъ. Cr 52,1	Марганецъ. Mn 55,0	Желѣзо. Fe 55,9 / Кобальтъ. Co 59 / Никкель. Ni 59 (Cu)
5		Мѣдь Cu 63,6	Цинкъ. Zn 65,4	Галлій. Ga 70,0	Германій. Ge 72,5	Мышьякъ. As 75	Селенъ. Se 79,2	Бромъ Br 79,95	
6	Криптонъ. Kr 81,8	Рубидій. Rb 85,5	Стронцій. Sr 87,6	Итрій. Y 89,0	Цирконій. Zr 90,6	Ніобій. Nb 94,0	Молибденъ. Mo 96,0	—	Рутеній. Ru 101,7 / Родій Rh 103,0 / Палладій. Pd 106,5 (Ag)
7		Серебро. Ag 107,93	Кадмій. Cd 112,4	Индій. In 115,0	Олово. Sn 119,0	Сурьма. Sb 120,2	Теллуръ. Te 127	Іодъ J 127	
8	Ксенонъ. Xe 128	Цезій. Cs 132,9	Барій. Ba 137,4	Лантанъ. La 138,9	Церій. Ce 140,2	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Иттербій. Yb 173	—	Танталъ. Ta 183	Вольфрамъ W 184	—	Осмій. Os 191 / Иридій. Jr 193 / Платина. Pt 194,8 (Au)
11		Золото. Au 197,2	Ртуть. Hg 200,0	Талій. Tl 204,1	Свинецъ. Pb 206,9	Висмутъ. Bi 208,5	—	—	
12	—	—	Радій Rd 225	—	Торій. Th 232,5	—	Уранъ. U 238,5		

Высшіе солеобразные окисды:

R	R²O	RO	R²O³	RO²	R²O⁵	RO³	R²O⁷	RO⁴

Высшія газообразныя водородныя соединенія:

				RH⁴	RH³	RH²	RH

Д. Менделѣевъ.
1869—1905.

Table 64 (P37)

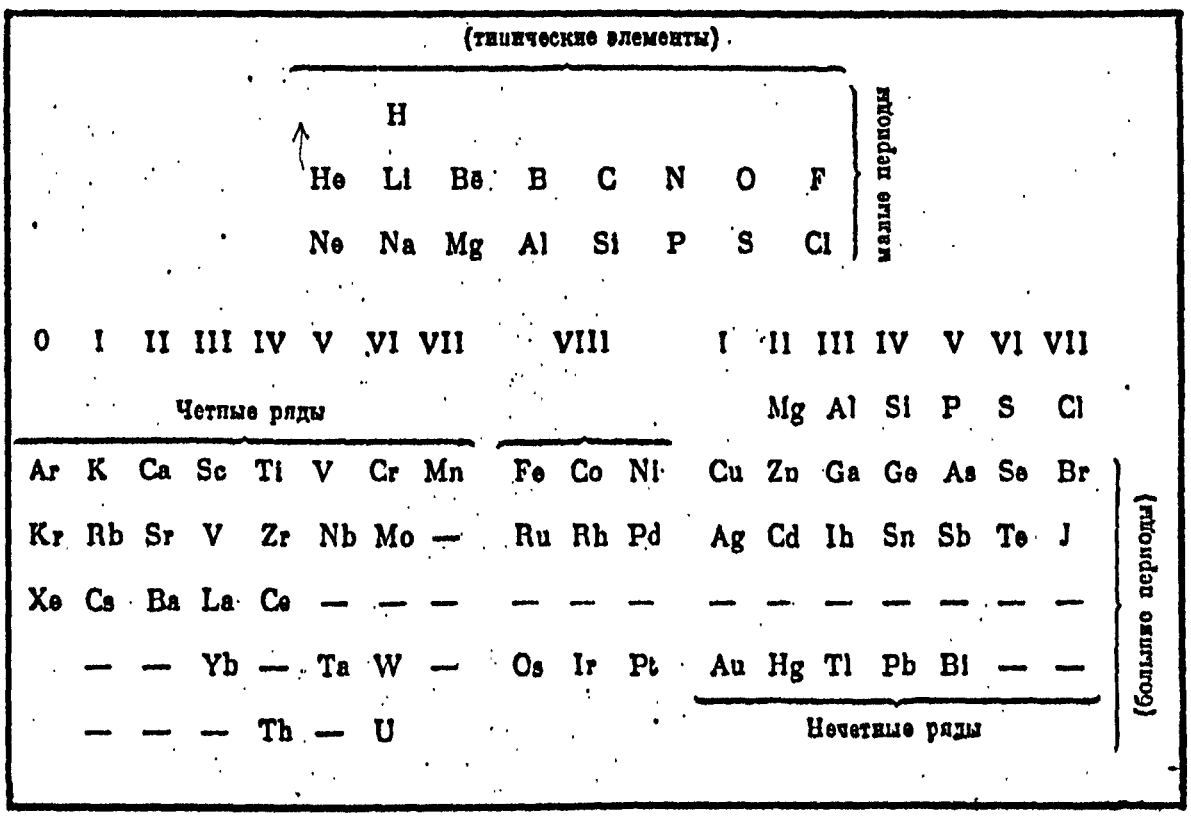
(типические элементы)
малые периоды
H
He Li Be B C N O F
Ne Na Mg Al Si P S Cl
0 I II III IV V VI VII VIII I II III IV V VI VII
Mg Al Si P S Cl
Четные ряды
Ar K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br
Kr Rb Sr V Zr Nb Mo — Ru Rh Pd Ag Cd Ih Sn Sb Te J
Xe Cs Ba La Ce — — — — — — — — — — — — — —
— — Yb — Ta W — Os Ir Pt Au Hg Tl Pb Bi — —
— — — Th — U
Нечетные ряды
(большие периоды)

Table65(P38)

CHAPTER V

MENDELEEV'S CONSIDERATION OF VARIOUS METHODS OF REPRESENTATION OF THE PERIODICITY OF THE ELEMENTS; OF THE QUESTION OF THE CAUSE OF THIS PERIODICITY; AND OF CERTAIN TYPES OF CHEMICAL AND PHYSICAL RELATIONSHIP WITHIN THE PERIODIC SYSTEM

A. Introduction

Many aspects of the periodicity of the elements continued to be discussed and developed by Mendeleev long after what we have recognised as the "era of discovery" of the periodic law (i.e. long after the publication in November 1871 of his article in Liebig's Annalen on "The periodic lawfulness of the chemical elements", G.); there were also certain aspects of this periodicity which Mendeleev did not (indeed, in some cases could not) even begin to discuss until some time after the era of discovery.

Mendeleev's use of the periodic system for changing or determining atomic-weight values, and for predicting the existence and properties of unknown elements, and his considerations on the placing of the rare-earth elements in the periodic system, formed an important part of his work on the periodic law both before and after late 1871; from the mid-1890's the problem of the relationship of the inert gases to the periodic system also occupied him. These topics will be considered in Chs. VI and VII. Other subjects with which Mendeleev began to be concerned during the period 1869-71, and which he continued to discuss and develop beyond merely this era of discovery, included: the various methods of (tabular, graphical and mathematical) representation of the periodicity of the elements; the question of the cause of this periodicity; the existence and nature of oxides, hydrides and organometallic compounds in relation to the structure of the periodic system; and horizontal, vertical and diagonal relationships within the short-form periodic table. These topics are considered in the present chapter.

A link between Mendeleev's consideration of the various methods of representing the periodicity of the elements (discussed in section B of the present chapter) and his views concerning the question of the cause of this periodicity (section C) was provided by the problem of the mathematical (functional) representation of the periodicity of the elements. His concept of "atomanalogy" in connection with the horizontal and vertical relationships within the periodic system (section D) provided Mendeleev with the basis for his attempts at interpolation and extrapolation of the periodic system (Ch.VI).

B. Mendeleev's consideration of various methods of representation of the periodicity of the elements

By far the most important aspect of Mendeleev's contribution to the classification of the elements on the basis of the periodic law was his construction of 2-dimensional arrangements of the elements by rows and columns - his "periodic tables". Throughout the time of his concern with the periodic law, i.e. from 1869 to 1906, Mendeleev published both long-form and short-form periodic tables. He presented horizontal long-form tables and vertical long-form tables; but apart from the horizontal table 10 (P3), published in May 1869, all of the (many) short-form tables published by him were of the vertical type. This preference by Mendeleev for the vertical orientation in the case of the short-form table was not discussed by him; it was probably based upon no more than aesthetic grounds. All of the short-form tables published by Mendeleev after 1870 (after table 15) presented a zig-zag arrangement of elements within the groups, indicating the sub-groups.

Having originally (March 1869) preferred the long-form arrangement of his "attempt at a system" (e.g. tables 8 and 9) to the short-form alternatives which he had considered at the time (such as table 10), Mendeleev seems by the end of 1869 to have come to prefer a short-form arrangement of the elements (as in tables 13-15). This preference for the short-form arrangement is clearly seen in the articles in which he first presented his "natural system" in late 1870-early 1871, especially in the article A natural system of the elements (R.), containing table 30 (see Ch.III). In his Annalen article published in November 1871, however, Mendeleev presented both a long-form table and a short-form table (tables 35 and 36 respectively), and this heralded the beginning of a second - and final - reversal of his preference in relation to the form of arrangement of the periodic table. By 1879 he had clearly developed a general preference for the long-form arrangement which he was not to lose: in this year he wrote, in reference to the vertical long-form arrangement in table 44, "The following mode of arrangement of the table of the elements gives, in my opinion, the possibility of best evaluating the periodic dependence".[1] In 1880 he said of table 45 - a horizontal long-form table - that it represents that form of arrangement of the elements "which I now consider to be the best and most complete expression of the harmony of the elements or the periodic law, and at the

[1] Moniteur Scientifique [3], 9 (1879) 692 (PLBA, 394).

same time the most convenient in the typographical respect";[2] and in a similar vein he wrote in 1898, referring to the horizontal long-form arrangement of table 56, "That form of arrangement given here is the original one, and seems to me to be the simplest and most graphic".[3] In his preference, from the 1870's on, for the long-form arrangement of the elements Mendeleev seems not to have distinguished between the horizontal and vertical forms of this arrangement.

Mendeleev's preference at any given time for the long-form or the short-form periodic table represented an overall judgment based upon a balancing of the particular advantages which he recognised in each type of arrangement. The main advantage which he felt the short-form table to possess over the long-form was the correspondence of the former to the "double periodicity"[4] of the highest valency of the elements in their "saline" oxides, bringing together the sub-groups of a group on the basis of the similarity of form of their compounds.[5] He undoubtedly also appreciated (although he does not appear to have acknowledged this explicitly) the convenience of the co-ordinate system of the short-form table for referring to the places of the elements in the periodic system. The main advantages of the long-form arrangement on the other hand were seen by Mendeleev in its correspondence to the periodicity of physical properties (e.g. atomic volume),[6] and its better indication of the closest analogies of the elements (i.e. within the sub-groups).[7]

In addition to expressing the periodicity of the elements in the form of periodic tables arranged in rows and columns according to the groups and series, or groups and periods, from 1889 Mendeleev also presented certain single-column or single-line lists of elements arranged according to increasing atomic weight with the series or periods somehow indicated along the sequence (see Ch. IV, n.6). An example of such a representation of

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[2]Berichte, 13 (188) 1803 (PLBA, 405). In the original Russian manuscript version of this article Mendeleev said of the table which came to be published as table 45 that it "now seems to me to be the most convenient of all for representing the essence of the periodic system" (see PLBA, 716).

[3]Bibl. 11, vol. 23, half-vol. 45, 1898, p.317 (PLBA, 254). By the "original" form of arrangement Mendeleev is referring to the form of arrangement of his original "attempt at a system" (e.g. table 8), i.e. horizontal long-form.

[4]This term "double periodicity" was not used by Mendeleev himself. It came into use later, e.g. see Zmaczynski, J.Chem.Ed.,14, part 5, 1937, p.233.

[5]See, for example, PLBA, 33 (1870) and PLBA, 81 (1871).

[6]See, for example, PLBA, 44 (1870) and PLBA, 257-8 (1898).

[7]See, for example, PLBA, 26 (1869).

periodicity from the 5th edition of Principles of Chemistry (1889), where this periodicity is indicated by marking off alongside the elements the values of their valencies with respect to hydrogen and with respect to oxygen, is given below (Fig.V-2).[8]

Already in his first article on the periodic law (Correlation of properties, 1869) Mendeleev spoke not only of planar arrangements of the elements by rows and columns, but also of "cubic" and "spiral" periodic systems (see Ch.III, pp.165-6). Just what he meant here by a "cubic" system is not at all clear from the text: did he, for example, mean strictly cubical (as had been the case for Kremers' 27-member cubic triads of 1856), or perhaps only cuboidal (as was van den Broek's so-called "cubiform" system of 1911[9]), or, possibly, nothing more than simply 3-dimensional? I have found no reference elsewhere by Mendeleev to a "cubic" classificatory system of the elements. However, there is one factor which perhaps has a bearing upon this matter, and which leads me to suggest tentatively that in referring in Correlation of properties to a "cubic" system Mendeleev may have had in mind a cubiform spiral arrangement (see Fig.V-1): this factor is that in the manuscript dating from early 1871 which is presented in Ch.IV as table 29(M20), the diagrams in the left-hand section appear to represent an attempt by Mendeleev to construct a cubiform spiral arrangement of the elements.

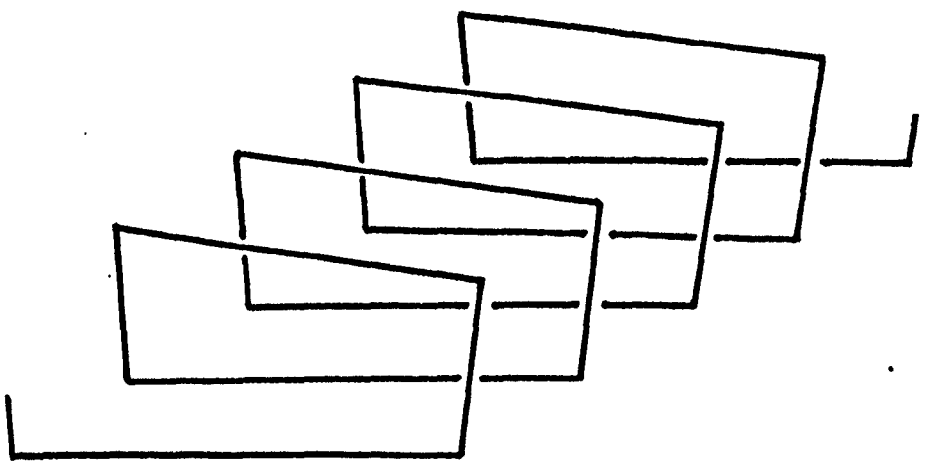

Fig.V-1.

Cubiform spiral.

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[8] Pr.Ch., R-5 (1889), folding sheet between pp.464 and 465.

[9] A. van den Broek, Phys. Z., 12 (1911) 490 (see Spronsen, Bibl.110, pp.187-8).

Періодичность химическихъ элементовъ.

Простыя тѣла и ихъ свойства.					Формы водородныхъ и металлоорганическихъ соединеній.		Элементы		Формы солеобразныхъ окисловъ.		Свойства высшихъ солеобразныхъ окисловъ.			
	t	a	s	A/s	RH^n и R(CH^3)^n		R	A	R^{1}O^n		s'	(2A − n·16)/s'	A	
	[1]	[2]	[3]	[4]		[5]		[6]		[7]		[8]	[9]	[10]	[11]
Водородъ	<−200°	—	<0,05	>20		n= 1	H	1	1	n=	0,917	19,6	<−20	1[a]
Литій	180°	—	0,59	12			Li	7	1†		2,0	15	−9	2[a]
Берилій	(900°)	—	1,64	5,5			Be	9	— 2		3,06	16,3	+ 2,6	
Боръ	(1300°)	—	2,5	4,4		3 — —	B	11	— — 3		1,8	39	10	
Уголь	>(2500°)	—	<2,0	> 6	4 — — —		C	12	— — — 4		>1,0	<88	<19	
Азотъ	−203°	—	<0,7	>20		3 — —	N	14	1 — 3* — 5*		1,64	66	< 5	
Кислородъ	<−200°	—	<1,0	>16		2 —	O	16			—	—	—	
Фторъ	—	—	—	—		1	F	19			—	—	—	
Натрій	96°	071	0,98	23		1	Na	23	1†		Na^{2}O	2,6	24	−21	3[a]
Магній	800°	027	1,74	14		2 —	Mg	24	— 2†			3,6	22	− 3	
Алюминій	600°	023	2,6	11		3 — —	Al	27	— — 3		Al^{2}O^3	4,0	26	+ 1,3	
Кремній	(1200°)	008	2,3	12	4 — — —		Si	28	— — 3 4			2,65	45	5,2	
Фосфоръ	44°	128	2,2	14		3 — —	P	31	1 — 3* 4* 5*			2,39	59	6,2	
Сѣра	114°	067	2,07	15		2 —	S	32	— 2 — 4* 5* 6*			1,96	82	8,7	
Хлоръ	−75°	—	1,3	27		1	Cl	35½	1 — 3 — 5* — 7*			—	—	—	
Калій	58°	084	0,87	45			K	39	1†			2,7	35	−55	4[a]
Кальцій	(800°)	—	1,6	25			Ca	40	— 2†			3,15	36	− 7	
Скандій	—	—	(2,5)	(18)			Sc	44	— — 3†			3,86	35	(0)	
Титанъ	(2500°)	—	(5,1)	(9,4)			Ti	48	— — 3 4			4,2	38	(+5)	
Ванадій	(2000°)	—	5,5	9,2			V	51	— 2 3 4 5			5,49	52	6,7	
Хромъ	(2000°)	—	6,5	8,0			Cr	52	— 2 3 — — 6*			2,74	73	9,5	
Марганецъ	(1500°)	—	7,5	7,3			Mn	55	— 2† 3 4 — 6* 7*			—	—	—	
Желѣзо	1400°	012	7,8	7,2			Fe	56	— 2† 3 — — 6*			—	—	—	
Кобальтъ	(1400°)	013	8,6	6,8			Co	58½	— 2† 3 4			—	—	—	
Никкель	1350°	017	8,7	6,8			Ni	59	— 2† 3			—	—	—	
Мѣдь	1054°	029	8,8	7,2			Cu	63	1† 2†		Cu^{2}O	5,9	24	9,8	5[a]
Цинкъ	433°	—	7,1	9,2		2 —	Zn	65	— 2†			5,7	28	4,8	
Галлій	30°	—	5,96	12		3 — —	Ga	70	— — 3		Ga^{2}O^3	(5,1)	(36)	(4,0)	
Германій	900°	—	5,47	13	4 — — —		Ge	72	— 2 — 4			4,7	44	4,5	
Мышьякъ	500°	006	5,7	13		3 — —	As	75	— — 3 — 5*			4,1	56	6,0	
Селенъ	217°	—	4,8	16		2 —	Se	79	— — — 4 — 6*			—	—	—	
Бромъ	−7°	—	3,1	26		1	Br	80	1 — — — 5* — 7*			—	—	—	
Рубидій	39°	—	1,5	57			Rb	85	1†			—	—	—	6[a]
Стронцій	(600°)	—	2,5	35			Sr	87	— 2†			4,3	48	−11	
Иттрій	—	—	(3,8)	(26)			Y	89	— — 3†			5,05	45	(−2)	
Цирконій	(1500°)	—	4,1	22			Zr	90	— — — 4			5,7	43	− 0,3	
Ніобій	—	—	7,1	13			Nb	94	— — 3 — 5*			4,7	57	+ 6,2	
Молибденъ	—	—	8,6	12			Mo	96	— 2 3 4 — 6*			4,4	65	6,8	
							(1)								
Рутеній	(2000°)	010	12,2	8,4			Ru	103	— 2 3 4 — 6 — 8			—	—	—	
Родій	(1900°)	008	12,1	8,6			Rh	104	— 2 3 4 — 6			—	—	—	
Палладій	1500°	012	11,4	8,3			Pd	106	1† 2 — 4			—	—	—	
Серебро	950°	019	10,5	10			Ag	108	1†		Ag^{2}O	7,5	31	11	7[a]
Кадмій	320°	031	8,6	13		2 —	Cd	112	— 2†			8,15	31	2,5	
Индій	176°	046	7,4	14		3 — —	In	113	— 2 3		In^{2}O^3	7,18	38	3,7	
Олово	230°	023	7,2	16	4 — — —		Sn	118	— 2 — 4			6,95	43	2,8	
Сурьма	432°	012	6,7	18		3 — —	Sb	120	— — 3 4 5			6,5	49	2,6	8[a]
Теллуръ	455°	017	6,4	20		2 —	Te	125	— — — 4 — 6*			5,1	64	4,7	
Іодъ	114°	—	4,9	26		1	J	127	1 — 3 — 5* — 7*			—	—	—	
Цезій	27°	—	1,88	71			Cs	133	1†			—	—	—	
Барій	—	—	3,75	36			Ba	137	— 2†			5,1	60	— 6,0	
Лантанъ	(600°)	—	6,1	23			La	138	— — 3†			6,5	50	+ 1,3	
Церій	(700°)	—	6,6	21			Ce	140	— — 3 4			6,74	50	2,0	
Дидимій	(800°)	—	6,5	22			Di	142	— — 3 — 5			—	—	—	
							(14)								
Иттербій	—	—	(6,9)	(25)			Yb	173	— — 3			9,18	43	(−2)	10[a]
							(1)								
Тантанъ	—	—	10,4	18			Ta	182	— — — — 5			7,5	59	4,6	
Вольфрамъ	(1500°)	—	19,1	9,6			W	184	— — — 4 — 6			6,9	67	8	
							(1)								
Осмій	(2500°)	007	22,5	8,5			Os	191	— — 3 4 — 6 — 8			—	—	—	
Иридій	2000°	007	22,4	8,6			Ir	193	— — 3 4 — 6			—	—	—	
Платина	1775°	005	21,5	9,2			Pt	196	— 2 — 4			—	—	—	
Золото	1045°	014	19,3	10			Au	198	1 — 3		Au^{2}O	(12,5)	(33)	(13)	11[a]
Ртуть	−39°	—	13,6	15		2 —	Hg	200	1† 2†			11,1	39	4,5	
Таллій	294°	031	11,8	17		3 — —	Tl	204	1† — 3		Tl^{2}O	(9,7)	(47)	(4,3)	
Свинецъ	326°	029	11,3	18	4 — — —		Pb	206	— 2† — 4			8,9	53	4,3	
Висмутъ	268°	014	9,8	21		3 — —	Bi	208	— — 3 — 5			—	—	—	
							(5)								
Торій	—	—	11,1	21			Th	232	— — — 4			9,86	54	6,0	12[a]
							(1)								
Уранъ	(800°)	—	18,7	13			U	240	— — — 4 — 6			(7,2)	(80)	(9)	
	[1]	[2]	[3]	[4]		[5]		[6]		[7]		[8]	[9]	[10]	[11]

> значитъ, что дѣйствительное число болѣе написаннаго. < значитъ, что дѣйствительное число менѣе того, которое написано.

[1] Температуры плавленія 4 простыхъ тѣлъ, считая для платины (=1775) (Violle). Температуры, обрабатываемыя двѣ числовыхъ таблицы (конц отнорительно), заключены въ скобкахъ.

[2] Средній коэффиціентъ о линейнаго расширенія твердыхъ простыхъ тѣлъ отъ 0° до 100°, принятаго согласно по данныхъ Фаи. Числа даны въ показателяхъ десять. Напр., 128 значитъ среднее расширеніе на 1° одного метра на 0,000128 метра.

[3] Удѣльный вѣсъ простыхъ тѣлъ въ твердомъ или жидкомъ состояніи. Въ скобкахъ написаны тѣ числа, до сихъ поръ не наблюденные, но обратные по положенію періодическаго закона. Тоже значеніе относится къ столбцамъ 4, 8, 9 и 10, гдѣ по наблюденнымъ цифрамъ даны въ скобкахъ.

[4] Среднее удѣльные объемы атомовъ простыхъ тѣлъ въ твердомъ и жидкомъ состояніяхъ; получаются дѣленіемъ A на s.

[5] Удѣльное выраженіе состава частицъ (объемъ пара = объему H^2) водородистыхъ и металлоорганическихъ соединеній, образуемыхъ элементами, причемъ, если элементъ даетъ нѣсколько водородистое соединеніе данной формы, тѣмъ и металлоорганическое, то число выражаетъ нормальный предѣлъ, если же водородистое соединеніе неизвѣстно, то — обыкновенный. Напр., при Sb отмѣтка 3 нормальнаго предѣла, это значитъ, что извѣстенъ SbH^3, Sb(CH^3)^3, Sb(C^{2}H^5)^3 и т. д. При Pb число 4 простыхъ предѣловъ показываетъ, что извѣстенъ Pb (CH^3)^4, Pb (C^{2}H^5)^4, но водородистый соединеній не извѣстенъ.

[6] Между знаками элементовъ и ихъ атомными вѣсами оставлено свободнымъ строки и поставлены знаки ——— и числа, показывающія количество неизвѣстныхъ по періодической системѣ промежуточныхъ элементовъ. Такъ отъ Di до Yb не достаетъ 14 элементовъ. Вѣроятно, что извѣстные изъ рядовъ элементовъ, нынѣ открытыхъ, но еще недостаточно изслѣдованныхъ, входятъ въ этотъ промежутокъ.

[7] Условное выраженіе состава солеобразныхъ окисловъ, образующихъ основанія, кислоты и соли (поэтому окислы CO или RO^2, какъ прямо не дающіе, не отмѣтили здѣсь всѣхъ возможностей). Для удобства сравненія, поставлены всѣхъ окисловъ высшихъ предѣловъ RO^n, будь и неизвѣстенъ отъ 1 до 8. Поэтому, такъ какъ противу Au отмѣтъ цифры 1 и 3, то это значитъ, что нынѣ даетъ окислы Au^{2}O и AuO^3, противу Pb отмѣтъ 2 и 4, значитъ извѣстны PbO и PbO^2 или PbO^2. Нормальный предѣлъ показателенъ окислы, данныя ими и извѣстные въ отдѣльныхъ состояніяхъ, какъ Au^{2}O^3, PbO, PbO^2 и т. д. Напр., при S отмѣтъ цифры 2, 4, 5, 6, показываютъ, что окислы SO^2 и SO^3 или SO^3 и SO^4 извѣстны и въ отдѣльномъ состояніи и въ соляхъ. Окисловъ же SO, отдѣльно не существуетъ, хотя гидратъ H^{2}SO^2 и соли дитіоновой кислоты; формы SO^3 отмѣчаетъ только образовательныхъ солей M^{2}SO^3. Знакъ †, поставленный при числѣ, показываетъ, что окислъ даннаго состава обладаетъ свойствами сильныхъ или почти сильныхъ основаній, а знакъ * отмѣтъ предѣлъ, дающій энергическія кислоты.

[8] Удѣльный вѣсъ s' высшихъ солеобразныхъ окисловъ въ твердомъ состояніи. Такъ, напр., число, стоящее противу W, относится WO^3, или WO^4.

[9] Объемъ этихъ высшихъ солеобразныхъ окисловъ, считая изъ формулы, (для удобства сравненія) RO^n. Числа эти получены дѣленіемъ числа 2 A − n· 16 (это есть, отвѣчающій формулѣ R^{2}O^n) на удѣльный вѣсъ s', данный въ предшествующемъ столбцѣ.

[10] Объемъ газа кислорода въ высшихъ окисл. Величина этого объема Δ находится чрезъ вычитаніе удѣльнаго объема простыхъ тѣлъ (столбецъ 4) изъ объема (столбецъ 9) высшаго окисла RO^n, равнаго отъ разности на число атомовъ кислорода n въ высшемъ окислѣ (изъ столбца 7). Отрицательныя величины показываютъ, что объемъ окисла меньше объема простого тѣла, въ немъ содержащагося.

[11] Нумерація малыхъ періодовъ (или рядовъ) для отдѣленія членовъ отъ членовъ.

1869 Д. Менделѣевъ.

Fig. V-2.

Mendeleev's reference in Correlation of properties to a "spiral" system is clearly to an arrangement of the elements in the form of a 3-dimensional (or "screw-shaped") spiral,  , developed from the planar table 10 (P3),[10] rather than to a 2-dimensional spiral,  . However, Mendeleev appears to have considered that a planar spiral system of the elements represents no significantly different arrangement from that of a screw-shaped spiral, as is seen particularly in his comments of late 1870-1871 concerning a 2-dimensional spiral system which had been published in 1870 by Baumhauer.[11] Thus, included among the extensive manuscript modifications which Mendeleev made in the early spring of 1871 to an off-print of his Correlation of properties were the following two sentences, introduced immediately after the statement in Correlation of properties that, "A spiral system is obtained": "This was stated in 1869, and was reproduced exactly in 1870 by Heinrich Baumhauer in the brochure 'Die Beziehungen zwischen den Atomgewichte/, Braunschweig-Vieweg 1870. The basic principle and methods are exactly the same as mine".[12] In his article On the question of the system of the elements (G.), published shortly afterwards (spring 1871), Mendeleev not only claimed priority over Baumhauer regarding the spiral system - "Mr. Baumhauer even uses the spiral arrangement of the elements which was mentioned by me" - but also remarked that such a spiral arrangement is "of little use and rather artificial".[13] This latter comment is probably a reflection of Mendeleev's failure in early 1871 to draw up a satisfactory spiral arrangement of the elements: as may be seen from table 29 (M20), he had attempted to construct both 2-dimensional and 3-dimensional spiral systems at this time (the 3-dimensional attempts appearing to be cubiform). Nevertheless, later in the same year Mendeleev was to remark in connection with the classification of the elements according to the periodic law that "the entire distribution of the elements is in essence unbroken, and corresponds to some extent to a spiral function".[14]

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[10] Spronsen (Bibl.110, pp.135,220) refers to table 10 (P3) itself as Mendeleev's "spiral" or "screw-shaped" system, although strictly this table is only the planar starting-point for construction of the spiral type of system mentioned by Mendeleev in 1869.

[11] H.Baumhauer, Die Beziehungen zwischen den Atomgewichte und der Natur der chemischen Elemente, Braunschweig, 1870. Extracts in English translation are given in Venable, Bibl.124, pp.120ff. Baumhauer's spiral system (which is given by Spronsen in Bibl.110, p.141) can be seen as a development along the lines of the earlier circular systems of O.W.Gibbs (L845) and Hinrichs (1867) (see Ch.III).

[12] See Sc.Ar., 321.

[13] Op.cit., p.352 (PLBA, 391).

[14] The periodic lawfulness of the chemical elements (G.), Liebig's Annalen, 1871, p.158 (PLBA, 121).

Mendeleev mentioned spiral classificatory systems of the elements a number of times later in his life, but he never published any attempt of his own at drawing up such a system. In a lecture-course of 1889-90 he referred to both planar and screw-shaped spiral arrangements: "... it [sc. the periodic law] may be represented in the form of a spiral, where each turn will express a definite period. It may also be expressed in the form of a screw-shaped line, where each turn of the screw will represent a period".[15] In a review given in the 5th (1889) - 8th (1906) editions of his Principles of Chemistry of the various methods of representing the periodicity of the elements Mendeleev included the category of planar spirals but not that of 3-dimensional (screw-shaped) spirals; rather surprisingly he here listed de Chancourtois among those who had drawn up planar spirals (the others named by him in this connection - Baumhauer, Huth and Erdmann - indeed had constructed planar rather than 3-dimensional spirals).[16]

As regards representing the periodicity of the elements by a "periodic curve" - such as Lothar Meyer's atomic-volume curve of 1870 - where the atomic weights of the elements are marked off along the abscissa of a rectangular co-ordinate system, and the value of some property expressed on the ordinate, Mendeleev had mentioned the possibility of drawing up a "wave-like" periodic curve in a manuscript of March 1869, nine months before Meyer constructed his atomic-volume curve.[17] This manuscript suggestion by Mendeleev was not published; and no attempt by Mendeleev actually to draw up such a curve is known. In March 1870 Mendeleev referred favourably to Meyer's atomic-volume curve as "an eye-catching means of expressing ... complex relationships ...".[18] Although continuing to acknowledge the visual impact of such a curve, Mendeleev later (from ca.1889) came to criticise this type of representation of the periodicity of the elements for its lack of discreteness: "This method, although graphic, has the theoretical disadvantage that it in no way indicates the existence of a definite number of elements in each period".[19]

Other graphical representations of the periodicity of the elements mentioned by Mendeleev included those based upon "atomicity" (valency) which

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[15] Bibl.75, p.157.

[16] See, for example, Pr.Ch., R-8 (1906) 615 (PLBA, 319).

[17] See Ch.III, p.163.

[18] See Ch.III, p.171.

[19] Pr.Ch., R-8 (1906) 615 (PLBA, 319).

had been proposed by Reynolds, Haughton and Crookes,[20] and that proposed by Rantsev which utilised the points of intersection of various surfaces.[21]

Mendeleev also considered the question of the mathematical (functional) expression of the periodicity of the elements.

In a manuscript vertical short-form periodic table dating from late 1870, table 23 (M16), Mendeleev wrote at the foot of the column containing the group IV sub-group C, Ti, Zr, Ce, Di and Th the expression, $12 + 36x + 1.7x^2$. This is evidently an expression for the atomic weights of the elements of this sub-group, with x being equal to half the value of the number given in table 23 (M16) to designate the particular series in which a given member of the sub-group is found (the series number of the row Na - Cl being 1, and so on).[22] As an attempt to correlate algebraically the atomic weights of chemically analogous elements this contribution by Mendeleev represents a continuation of the tradition of the 1850's, although the fact that the value of x in this expression reflects the series-number of the elements in the short-form periodic table renders the expression less arbitrary than those which had been given by Cooke, Dumas, Sokolov, etc., during the 1850's; however, the significance of the form of the expression given by Mendeleev, and of the particular values of the constants 36 and 1.7, is unclear. Also in table 23 (M16) we find the formulae ClO^3, SO^2 and PO included in the places containing Rb (I-4), Zn (II-3) and 44 (III-2, corresponding to the undiscovered Sc) respectively. Of these three formulae only SO^2 corresponds to a compound known to Mendeleev (viz. sulphur dioxide); PO is still not known to exist, and ClO^3 (Cl^2O^6) has been discovered only since Mendeleev's death. The significance of these formulae seems therefore to lie not in the representation of real compounds, but elsewhere; of relevance in this connection is undoubtedly the fact that the "molecular" weight of each "oxide" is approximately equal to the atomic weight of its host element in table 23 (M16):

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[20] On the systems of Reynolds, Haughton and Crookes, see Spronsen, Bibl.110, pp.179, 224, 225. Mendeleev criticised these systems on the grounds of the particular values of valency which they assumed.

[21] Mendeleev refers to Rantsev's proposal in, for example, Pr.Ch., R-8 (1906) 616 (PLBA, 320). Rantsev appears not to have published his system.

[22] See Kedrov, Sc.Ar., 824-5.

Host element	"Oxide"
Rb = 85	ClO^3 = 83.5
Zn = 65	SO^2 = 64
44	PO = 47

The question of the significance of Mendeleev's inclusion of the above three oxide-formulae in table 23 (M16) has been considered by Kedrov, who writes:

> ... with the transition from gp. I to II to III in the cells [sc. places in the periodic table] in which the insertions are made, a transition from gp. VII to VI to V is accomplished in the elements which are inserted into these cells; ... the sum of the group-number of the cell in which the insertion is made and the group-number of the element which is inserted, is 8 ...
>
> We shall indicate the element of the cell in which the insertion is made by the letter R (without an index) and its co-ordinates by x, y. We note that x + y = 5 ...
>
> Further, we shall indicate by R′ the element whose "oxide" is inserted into the cell of element R, and its co-ordinates correspondingly by x′, y′. We note that y′ = 1 ... It is evident that both straight lines (x + y = 5, and y′ = 1) cross at the "point" x = 4, y = 1, i.e. in the cell (the "place") of silicon.
>
> We note, in addition, that x + x′ = 8. We may therefore say that the element R′ is complementary to the element R. It appears that D.I. [Mendeleev] was attempting to find the dependence between the value of the atomic weight P of element R - expressed by means of the co-ordinates of its "place" (x, y) - and the value of the atomic weight P′ of element R′, expressed by means of the co-ordinates of its place (x′, y′). This dependence may be expressed, such that the atomic weight of element R is equal to the weight of the oxide $R'O^n$ where n = 4 - x, as:
>
> $$P = P' + (4 - x)16 \qquad (1)$$
>
> (here 16 is the atomic weight of oxygen) ...
>
> Since x + y = 5, expression (1) may be rewritten as:
>
> $$P = P' + (y - 1)16 \qquad (2)$$
>
> The atomic weight P of element R is here presented as a function, a) of its "place" (abscissa x or ordinate y) in the system, and b) of the atomic weight (P′) of the element R′ complementary to it. But we have found no such equation given by D.I. himself, although it appears to be just this equation which underlies the notes [sc. insertions of $\underline{ClO^3}$, $\underline{SO^2}$, $\underline{PO}$] by D.I. which we have been examining, and only it alone may explain their significance.[23]

It is certainly possible that, as Kedrov suggests here, the insertion of the formulae $\underline{ClO^3}$, $\underline{SO^2}$ and $\underline{PO}$ into the places occupied by Rb, Zn and $\underline{44}$ in table 23 (M16) signifies an attempt by Mendeleev "to find the dependence between the value of the atomic weight P of element R ... and the value of

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[23] Sc.Ar., 823-4.

the atomic weight P′ of element R′" in terms of the co-ordinates of R and R′. On the other hand, Mendeleev's motivations and aspirations may have been rather less generalising and coherent.

In 1871, in his article on The periodic lawfulness of the chemical elements (G.), Mendeleev spoke of the lack of knowledge of the precise functional dependence of the physico-chemical properties of the elements upon atomic weight, and pointed out that superimposed upon the fundamental periodic form of this dependence is a fine structure of "individual" perturbations, which he related to the deviations from strict regularity in the atomic-weight differences in the periodic table:

> ... the atomic-weight differences for the corresponding members of the different groups and series are far from being equal, even within the limits of experimental error. Thus ... Na - Li = 16, whereas the difference Mg - Be = 14.6; the difference K - Na = 16, but Ti - Si = 20, V - P = 20 ...
>
> We must therefore recognise in the atomic-weight values of the elements a similarity or closeness of differences for corresponding members, and individual deviations which make these differences not completely equal. In precisely the same way it is necessary to distinguish for the elements their general properties, which are in periodic dependence upon atomic weight (for example, the faculty for giving certain forms of oxidation ...), and their individual properties, which depend upon the above-mentioned deviations.[24]
>
> Because at present this very dependence (function) is unknown to us, only one of its properties - periodicity - being known, then at present there is no possibility of determining the magnitude of these deviations, and therefore there is no possibility of correcting the magnitude of the atomic weights precisely; we may only indicate

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[24] In the Russian manuscript version of this article Mendeleev had originally continued this paragraph with the following remarks, which he subsequently crossed out (see Sc.Ar., 452):

"This may be expressed by the following formula. X denotes a property of the elements, P denotes atomic weight, and φ denotes the periodic dependence of properties upon atomic weight: $X = \varphi P$ is the expression of the periodic dependence. For certain properties, which can change only periodically, this expression will denote precisely the periodic lawfulness; if we separate a small portion p from P, then the precise expression will be, $X = \varphi(P - p)$. The capacity for combination with H, O, etc. is such a periodic property, because combinations are accomplished only in multiple proportions, by leaps. For other properties, which can undergo continuous change, the expression will correctly be: $X_1 = \varphi_1(P - p)$."

narrow limits, within which the atomic weight of a given element must be found.[25, 26]

In his Faraday Lecture, 1889, Mendeleev discussed certain attempts which had been made at obtaining a functional representation of the periodic law. He rejected the continuous trigonometrical functions proposed by Rydberg and Flavitskii, on the grounds that "the periods of the elements present ... points, numbers, sudden changes of mass, and not a continuous development".[27] He continued:

> Only in the "theory of numbers" are the problems similar to those we are faced with here [sc. in the case of the periodic law]. Two of the attempts at algebraically expressing the atomic weights of the elements seem worthy of attention, although neither can be considered complete, or as promising to solve finally the problem of the periodic law. The attempt of E.J. Mills (1886) does not even aspire to this end; this author considers that all atomic weights of the elements are expressed by the exponential function,
>
> $$15(n - 0.9375^{t}),$$
>
> where n and t vary as whole numbers ... The other attempt, made by B.N. Chicherin (1888), places the problem of the periodic law in the first rank, but has so far been applied only to the alkali metals. Chicherin has pointed out ... that the atomic volumes of all the alkali metals ... can be represented by the formula,
>
> $$A(2 - 0.00535\ An),$$
>
> where A is the atomic weight, and where n = 8 for Li and Na, 4 for K, 3 for Rb and 2 for Cs.[28]

In his article of 1898 on The periodic lawfulness of the chemical elements (R.) Mendeleev reiterated certain of the views he had expressed earlier concerning the question of the functional representation of the

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[25] It is clear from the paragraph immediately following this one in Mendeleev's article, where the question of the atomic weight of Te is discussed ("tellurium, judging from the periodic law, must have an atomic weight greater than Sb = 122 and less than I = 127"), that the "limits" to which Mendeleev here refers, within which the atomic weight of a given element must be found, are the atomic-weight values of the immediate neighbours of the element in the periodic system. Mendeleev was not prepared to tolerate exceptions to the principle of atomic-weight ordering in the periodic system (See Ch.VI, on Mendeleev's use of the periodic system for modifying and determining atomic-weight values).

[26] Op.cit., pp. 208-9 (PLBA, 159-60).

[27] PLBA, 216.

[28] Ibid., 217-8.

periodic law, and remarked upon the significance which he felt a precise functional representation of the periodic law would have for the explanation of the cause of this law, and for the elucidation of the nature of the chemical elements:

> ... the most important of all [sc. of the general questions raised by the periodic law] is, I think, that of the precise correlation between the numbers expressing the atomic weights of the elements, their place in the system, and the special (individual) properties of the elements; because with all the parallelism of the properties of the elements, there is no uniformity in the relationships of atomic-weight values, either arithmetical or geometrical. Thus, for example, taking O = 16 ... the differences Si - C = 16.39, S - O = 16.07 and Cl - F = 16.39, which are not identical; it is impossible to think that S = 32.39, as might be supposed if equality of differences be assumed ... In the geometrical ratios ... ungeneralised inequalities of the very same kind are shown, the cause of which, it seems to me, may in due course (when we know more precisely than we do at present the atomic-weight numbers, and the possible error in their determination) be confronted, and then connected by a law with the individual peculiarities of the elements. Already many investigators - especially Rydberg, Bazarov, Haughton, Chicherin, Flavitskii, Mills, and others - have tried, from various sides, to find a precise expression of the periodic law, but this subject has so far not been amenable to precise and general deductions, although it promises very much not only for the increase in degree of precision of our knowledge of atomic weights, but also for our understanding of the cause of the periodic law, and so of the very nature of the elements. In this connection I consider it necessary to turn attention to that frequently overlooked fact that an ordinary "continuous" function, e.g. a sine function, may not serve as an expression of the periodic law, because the elements are characterised above all by "breaks", as is evident for example from the fact that between K = 39 and Ca = 40 it is impossible, without violating Dalton's law (of whole multiple proportions in the number of atoms, e.g. KCl and $CaCl_2$), to conceive of an unlimited number of intermediates [or even one intermediate - JRS], since there is no intermediate whole number between 1 and 2. Therefore it seems to me that for the periodic law we may seek either a geometrical expression in the points of intersection of two "continuous" curves or an analytic expression in the "theory of numbers" ... The absence so far of a strict analytic expression for the periodic law, is, in my opinion, determined by the fact that this law concerns a field which is still very new to mathematical treatment. As regards the absence of any explanation of the essence of the periodic law, the reason for this should be looked for above all in the absence of a precise expression for it.[29]

Mendeleev discussed various attempts which had been made at obtaining a functional representation of the periodic law also in the 5th (1889) - 8th (1906) editions of Principles of Chemistry, emphasising throughout

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[29] Bibl.11, vol. 23, half-volume 45, 1898, p.323 (PLBA, 271-3).

that a successful function in this respect cannot be continuous. In the 8th edition he still acknowledged that attempts in this direction "have not yet led to the desired results".[30, 31]

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[30] Pr.Ch., R-8 (1906) 616 (PLBA, 321).

[31] Attempts at a mathematical representation of the periodicity of the elements which have been made since Mendeleev's death include those by Hsueh and Chiang, Bibl.27 (1937), and Trifonov, Bibl.120 (1971). Trifonov's work includes also an historical survey of the various attempts which have been made in this direction since the time of the discovery of the periodic law.

C. Mendeleev on the question of the cause of the periodicity of the elements

> [1871] ... despite all the apparent simplicity of the affair, we have as yet no possibility of maintaining any kind of hypothesis which adequately explains the law of periodicity.[32]

> [1889] Two centuries have elapsed since the birth of the conception of gravity, and while we do not yet understand its cause it must nevertheless be considered as fundamental to natural philosophy ... The periodic doctrine of the elements is only twenty years old; it is hardly surprising that knowing nothing of the cause of either gravity or mass, or of the nature of the elements, we do not understand the cause of the periodic law. It is only by accumulating well-tried laws ... that we may hope little by little to lift the veil which conceals from us the causes of the secrets of nature, i.e. to uncover their mutual connection.[33]

> [1898] We do not know the explanation of the cause of the periodic law. But we must not forget that it is less than 30 years since its discovery, and that the law of gravitation, which was discovered more than 200 years ago and which has paramount significance in science, is still not explained in its essence. It is used, and used legitimately; so also the periodic law may and should be used, although its cause also is not clear. We can hope that in time the cause will be found; but in the meantime it is better to work hard in elaborating the subject, because from this the sum of our knowledge of the elements indirectly increases.[34]

> [1906] It is the general feeling that it is too early to explain ... the periodic law ... But just as the law of gravity can be used without knowing the cause of gravity, so also the laws discovered by chemistry can be used for chemical purposes without having an explanation of their cause.[35]

The above extracts from Mendeleev's writings show his recurring acknowledgment, throughout the time of his concern with the periodicity of the elements, of the absence of an explanation of the cause of the periodic law. Also shown is his insistence that despite the inability of scientists yet to explain its cause, the periodic law still had immense, and fundamental, value in chemistry, just as the unexplained Newtonian law of gravitation had in physics.

While acknowledging the absence of any adequate explanation of the cause of the periodic law, Mendeleev did make certain remarks which give some indication of his views concerning the possible direction such an

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[32] Pr.Ch., R-1, part II (1871) 834 (PLBA, 380-1).

[33] Faraday Lecture: PLBA, 225.

[34] The periodic lawfulness of the chemical elements (R.), Bibl.11, vol.23, half-vol. 45, 1898, p.318, footnote (PLBA, 258-9).

[35] Pr.Ch., R-8 (1906) 617 (PLBA, 321).

explanation might take and the types of appraoch which might prove fruitful in the search for such an explanation.

The idea that the periodicity of the properties of the elements might be merely "the result of chance", representing no more than a random variation of physico-chemical properties with increasing atomic weight, was explicitly rejected by Mendeleev: "... although I have had my doubts about some obscure points [sc. in connection with the periodic law], I have never once doubted the universality of this law, because it could not possibly be taken to be the result of chance".[36] This appears to be no more than an intuitive comment by Mendeleev: he shows no sign of having considered the objective validity of his claim.[37]

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[36] Pr.Ch., R-7 (1902-3) 467, n.15 bis (Colls., 2, 453); R-8 (1906) 619, n.411 (PLBA, 326). Mendeleev's rejection of the "randomness" hypothesis for explaining chemical periodicity does not appear to have been made in response to anyone's actual support for such an hypothesis.

I have come across no-one who supported the "randomness" hypothesis for explaining the periodic law. The New York "Evening Post" of June 16, 1905, in a review of the 3rd English edition of Mendeleev's Principles of Chemistry says rather disparagingly that the periodic law "never was anything more than a rule of waviness", but there is no indication that by "waviness" was meant anything as extreme as "random fluctuation".

[37] An attempt at an objective evaluation of Mendeleev's claim that the periodic law "could not possibly be taken to be the result of chance" has been made by the present author, and will be published elsewhere. The results of this attempt support Mendeleev's intuitive assessment. Two different methods were used: a procedure analogous to the testing for randomness of what are known in statistics as "time-series" (a "time-series" being a chronologically-ordered set of observations of a numerical feature of an individual or a population), and a procedure which uses the idea of "chemical family". The fact that different properties of the elements show close parallels in the pattern of their fluctuation ("periodicity") with respect to atomic weight, i.e. that chemical families actually exist, was accepted as an empirically-given starting-point: what was tested was the null hypothesis that this particular common pattern of fluctuation ("periodicity") represents a random fluctuation. In testing the periodicity of the elements for randomness not only do we have no general mathematical expression (function) for this periodicity, but also we have to work with an empirically-given set of atomic weights for which there is no known overall generating formula; this latter fact is of particular significance in connection with the test which employs the concept of chemical family, resulting in the necessity for a somewhat lengthy and laborious series of determinations from the individual empirical atomic-weight values. The test based upon the theory of time-series was the so-called "turning-point test", which involves comparing the number of turning-points (i.e. maxima and minima) of the series with the calculated number for a random series of the same number of terms. To make use of the concept of chemical family in testing the periodicity of the elements for randomness we must compare for different families such characteristics as the number of members, the values of the intervals between consecutive members, and the sequence of such values: the mere existence of chemical families is no indication of non-randomness in the (common) variation of different properties with increasing atomic weight.

Mendeleev saw the periodic law as providing a bridge linking those two phenomena of nature which as a working scientist he took pragmatically to represent the fundamental quantitative and qualitative aspects of matter, viz. mass (expressed as weight) and the chemical individuality manifested in the chemical elements.[38] This particular "bridging" view of the periodic law[39] is seen, for example, in a passage first given in the 7th (1902-3) edition of Principles of Chemistry, where Mendeleev presents an outline of what he claims to have been the general heuristic guideline which led him to his discovery of the periodicity of the elements:[40]

> Applying my energies to the study of substance, I see in it two such [sc. general and distinctive] signs or properties: mass, which occupies space, and evinces itself in gravity and - with greatest clarity or reality - in weight; and the individuality expressed in chemical transformations, which is most clearly

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[38] At the purely speculative level Mendeleev did not commit himself to the view that the empirical property mass (∝ weight) necessarily expresses the quantity of matter (see Ch.I), nor did he reject the possibility that the chemical elements may be composed of one or more simpler (primary) substances (see Ch.II).

[39] Mendeleev's view of the periodic law as a bridge at the level of empirical generalisation calls to mind certain general comments which he makes in the preface to the later editions of his Principles of Chemistry, where he likens science to a "suspension bridge" (visiachii most) of interlocking empirical laws over the "abyss" (bezdna, or propast') of the unknown, and expresses the hope that his book will encourage in the reader a curiosity "which will incline thought to confirm by experiment, and which will lead to the search for new threads for the construction of bridges across the abyss of the unknown" (see, for example, Colls., 24, 36-7, from Pr.Ch., R-7, 1902-3).

Mendeleev's "suspension bridge" view of science has been used by R.B. Dobrotin as a basis for his own ideas regarding the use of empirical generalisations as "models" in chemistry, e.g. see Nekotoryo metodologicheskie voprosy modelirovaniia v oblasti khimii, Dobrotin and V.A. Shtoff, in Filosofskie kategorii v estestvennonauchnom poznanii, Minsk, 1972; and Empiricheskie sootnosheniia sovremennoi khimii, Dobrotin, Moscow, 1974.

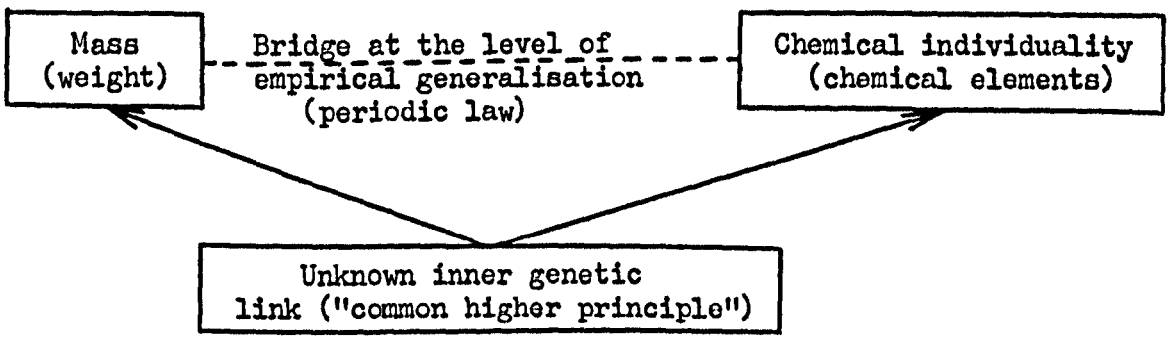
[40] From the evidence dating from the actual time of Mendeleev's discovery of the periodic law, the heuristic path presented in this passage from the 7th edition of Principles of Chemistry is almost certainly a rational reconstruction rather than a realistic account. The account which Mendeleev gives in his first article on periodicity - Correlation of properties, 1869 - is much more convincing, viz. that in his search for a "natural" classificatory system embracing all chemical elements (the motivation for this being primarily pedagogical) the attempts were based upon atomic weight because this was the only known suitable property of the elements (atomic weight is a property of the elements rather than of the free simple substances; it is a numerical property, and the value for each element appeared to be unique and invariant) (see Ch.III). But rational reconstruction or not, the passage quoted here from Principles of Chemistry nevertheless illustrates Mendeleev's view of the periodic law as a bridging link between mass and chemical individuality.

> formulated in the notion of chemical elements. When I think of substance, outside any idea of material atoms, I cannot avoid the two questions of how much substance and what kind of substance - to which correspond the conceptions of mass and chemism. The history ... of chemistry leads ... to the demand for recognition not only of the permanence of the mass of a substance, but also of the permanence of the chemical elements. Therefore the thought involuntarily arises that there must necessarily be some link between mass and the chemical features of the elements; and as the mass of a substance is ultimately expressed ... in its atoms, we should search for a functional correspondence between the individual properties of the elements and their atomic weights ... So I began to sort out ... elements with similar properties, and elements with close-valued atomic weights, which quickly led me to the conclusion that the properties of the elements stand in periodic dependence upon atomic weight.[41]

The link between mass (weight) and chemical individuality which was provided, at the level of empirical generalisation, by the periodic law, led Mendeleev to recognise the existence also of an unknown inner genetic link (a "common higher principle") between the nature of the chemical elements and the property of mass (weight):

> The properties of the atoms being a function of their weight, a multitude of conceptions which have been more or less consolidated in chemistry must be developed and cultivated in the sense of this result. Although at first sight it seems that the chemical elements are self-existent in their character and completely independent of each other, instead of this conception of the nature of the elements we must now set up the conception of the dependence of their properties on mass, i.e. see the subordination of the individuality of the elements to a common higher principle which evinces itself in gravity and in the majority of physico-mechanical phenomena.[42]

A schematic representation of Mendeleev's view of the relationship between mass (weight) and chemical individuality (the chemical elements) might therefore be -



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[41] Pr.Ch., R-7 (1902-3) 467, n.15 bis (Colls., 2, 452-3); R-8 (1906) 619, n.411 (PLBA, 325-6).

[42] Pr.Ch., R-6 (1895) 448-9. The same passage occurs in R-7 and R-8; a related earlier version is given in R-3 (1877) 852 and in R-4 and R-5. In connection with the reference at the end of the passage to "the majority of physico-mechanical phenomena", see Ch.I, n.17.

This view of the relationship between mass (weight) and the chemical elements led Mendeleev to see the question of the cause of the periodic law as being intimately connected not only with the question of the nature of the chemical elements, but also with the question of the nature of mass (weight). As early as 1871 he had the following to say on this subject:[43]

> This periodicity [sc. of the properties of the elements] at present is for us a most mysterious phenomenon ... It seems to me that an explanation is possible only in the sense of a dynamical presentation which is able to (and must) explain above all the very conception of weight. Only with a clear notion of weight is there a possibility, on the basis of atomic weight, of constructing an hypothesis about the nature of the elements; but this subject, as yet untouched upon, should not yet occupy us in such an exact science as chemistry, because the time has not yet arrived (although, in my opinion, it is not far away) when the cause of weight and attractions becomes as clear to us as the cause of light.[44]

Here we find some indication (albeit in extremely general terms) of the type of explanation which Mendeleev expected to be found for the cause of the periodic law (and for the nature of the chemical elements, and the nature of mass and weight), viz. an explanation by means of a "dynamical" theory.[45] There is no suggestion here or elsewhere in Mendeleev's writings that he was prepared to discard his matter-plus-motion ontological framework in which matter and motion provide the fundamental, distinct but necessarily concomitant, indestructible components of the substances of the world. But, as we have already seen (Ch.I, section A), the strict conservation assumed by Mendeleev for each of these fundamental components, matter and motion, did not preclude for him the possibility of non-conservation of weight: Mendeleev was prepared to acknowledge that weight might be a compound effect of matter-plus-motion, non-conservation of weight then being

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[43] For a later passage see, for example, the extract from Mendeleev's Faraday Lecture (1889) quoted at the beginning of this section (p.300).

[44] Pr.Ch., R-1, part II (1871) 834-5 (PLBA, 381-2).

[45] A few months earlier Mendeleev had already written, "When the periodic dependence of properties on atomic weight, and the atomological relationships of the elements, can be subordinated to precise laws, we will approach more closely to the very essence of the differences between the various elements, and chemistry will then be in a position to discard the statical ideas of the present time and take on that dynamical direction which has already proved so fruitful in the study of the majority of physical phenomena" (A natural system of the elements, R., 1871, p.56; PLBA, 101). (Mendeleev's concept of "atomology" or "atomanalogy" is discussed in section D of the present chapter).

viewed in terms of the conversion of a part of the "motion-component" of weight into some other form of motion which does not contribute to weight, or vice versa. Mendeleev thus allowed the possibility of non-proportionality of weight (or mass, in the purely pondero-inertial sense) and quantity of matter. The potential flexibility embodied in Mendeleev's restriction of possible explanatory theories of the periodic law to those which are "dynamic" rather than "static" was therefore extremely great.

Mendeleev's consideration of the question of the likely path by which an explanation of the cause of the periodic law might eventually be attained involved his discussion of the following general types of approach, reflecting (as would indeed be expected) the nature of his views outlined above on the relationship between mass and the chemical elements:-

i) Efforts directed towards determining the nature of mass (weight).

ii) Efforts directed towards determining the nature of the chemical elements.

iii) Consolidation and refinement of the periodic law itself - this constituting for Mendeleev an aspect not only of ii), but also of i).

Dealing first with Mendeleev's opinion of approach iii) as a means to attaining an explanation of the cause of the periodic law, we note that he made numerous general remarks to the effect that it is only by the accumulation and consolidation of empirical laws that we can hope to gain an insight into the inner causes of the phenomena of nature.[46] In the particular case of the periodic law, refinement of this law in the sense of expressing it as a mathematical function was seen by Mendeleev to be of major significance for attaining an understanding of its cause: "As regards the absence of any explanation of the essence of the periodic law, the reason for this should be looked for above all in the absence of a precise expression for it."[47]

In connection with approach ii), we have already seen (Ch.II) that in the light of the long history of "futile" attempts to demonstrate the complexity of the chemical elements Mendeleev tended (particularly after ca. 1880) to recommend that in the absence of any well-authenticated decomposition, synthesis or transmutation of the chemical elements, chemistry should treat the elements pragmatically as qualitatively-distinct

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[46] See, for example, the passage of 1889 quoted at the beginning of this section, p. 300.

[47] Bibl.11, vol.23, half-vol. 45, 1898, p.323 (PLBA, 273). This remark is part of the longer passage quoted earlier in the present chapter, p.298.

ultimate forms of matter. At the same time Mendeleev nevertheless felt that in fact the elements probably are composite entities; and he acknowledged that should a transmutation of the elements ever be demonstrated, then this would be likely to have great significance for the problem of the cause of the periodic law[48] - "If it were to be shown [sc. that the elements are not immutable]..., then we may gain the possibility of understanding the lawfulness which has been noticed for the elements, namely their periodicity"[49].

Approach i) to the problem of explaining the cause of the periodic law was considered by Mendeleev to be much more promising than approach ii), an opinion which he appeared to hold more strongly as time went by.[50] And whereas at first he gave no suggestion of possible approaches to solving the problem of the nature of mass or weight (apart, perhaps, from consolidation and refinement of the empirical periodic law), in the early 20th century he came to express the view that the path to a true understanding of mass lay via an understanding of the "ether". Thus whereas in 1889 Mendeleev had written, "The primary conception of ... mass ... belongs among those categories which the discipline of science has so far not allowed us to touch upon, because as yet we have no means of dissecting or analysing this conception",[51] in 1902 he wrote, "I think that before we understand mass a clear and real conception of the ether must be worked out".[52] Also in 1902 Mendeleev wrote:

> ... the more I have thought about the nature of the chemical elements, the more firmly have I turned away from the classical notion of primary matter, and from the hope of attaining the desired end [sc. an understanding of the nature of the elements] by a study of electrical and optical phenomena, and have come more and more urgently and clearly to realise that first and foremost are needed more concrete conceptions of "mass" and "ether" than we have at present.[53]

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[48] For an apparent difference between Mendeleev's attitude in the light of the periodic law towards the likelihoodon the one hand that the elements are composite entities, and on the other that they are composed of a single primary matter, see Ch.II, pp. 102-4.

[49] Gold from silver (R.): PLBA, 447. (A continuation of this passage is quoted on p. 103).

[50] Approach i) had been advocated by Mendeleev as early as 1871, as is seen from the passage quoted earlier in this section, p. 304. But it was advocated by him more strongly later (see below).

[51] Faraday Lecture: PLBA, 215.

[52] Attempt at a chemical conception of the world-ether (R.): PLBA, 502, footnote. The attempt by Mendeleev to provide a "chemical conception" of the ether did not, however, lead to any suggestion as to the nature of mass (see Ch.I, pp.43-4).

[53] Pr.Ch., R-7 (1902-3): Colls., 24, 42-3. A similar passage occurs in R-8 (1906): Colls., 24, 51.

We have already seen (Chs.I and II) that in connection with the problem of understanding the nature of the chemical elements Mendeleev saw no advantage over the idea of invariant ultimate chemical atoms in either the theory of the vortex atom or the subsequent ideas of an "electronic" structure of the atom. As regards the particular contribution of J.J. Thomson in 1904, which presented the germ of an explanation of the periodic law in terms of a structure of the chemical atom involving concentric rings of electrons "moving about in a sphere of uniform positive electrification",[54] it seems that Mendeleev was unaware of this development. He mentioned Thomson only in a completely general reference to the notion of electrons.[55]

Noretta Koertge (1968) has drawn the conclusion that "Mendeleev gives neither a satisfactory, unified account of what direction a possible explanation of the periodic law might take, nor heuristic arguments in favour of such an approach, nor detailed suggestions as to how to carry it out", pointing out at the same time the significance in Mendeleev's eyes of "mass" and Newtonian mechanics (or an extension thereof) for any approach to the solution of the problem of the cause of the periodic law.[56] While largely agreeing with Koertge's analysis of Mendeleev's position, I feel that it presents Mendeleev's approach to the problem of the cause of the periodic law as being slightly more negative and general than it actually was: no mention is made of his comments on the importance of obtaining a precise mathematical expression of the periodic law for understanding the cause of the law, or of his view towards the end of his life that the path to understanding the cause of the periodic law - and the nature of mass and the chemical elements - lies through an understanding of the nature of the ether. (These omissions, as also Koertge's presentation of Mendeleev as being firmly against the possibility of composite chemical elements, are however quite understandable in view of the fact (acknowledged by Koertge) that her analysis was based only upon such fairly limited material as is available in English translation.)

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[54] J.J. Thomson, Phil. Mag., [6], 7 (1904) 237.

[55] Pr.Ch., R-8 (1906) 483 (PLBA, 600): see Ch.II, p.98.

[56] Bibl.48, pp.274-94.

D. Mendeleev's discussion of certain types of chemical and physical relationship within the periodic system.

1. The nature of oxides and hydrides in relation to the structure of the periodic system.

In his article On the quantity of oxygen (R., publ.1870) Mendeleev had pointed out that the arrangement of groups in the short-form periodic table "is shown to comply with that order in which the elements are distributed according to the form of their limiting saline oxides", distinguishing "saline oxides" (solianye okisly), or "oxides ... which are capable of giving salts", from those oxides which "do not possess saline character and which constitute that class of oxides which are correctly called peroxides (perekisiami)".[57] He expanded upon this distinction between "saline oxides" and "peroxides" in a short paper entitled Zametka o perekisiakh (A note on peroxides) written in October 1871.[58] He wrote here:

> The conception of peroxides is lacking in definiteness if we include in their number not only H_2O_2, Na_2O_2, BaO_2, but also MnO_2, PbO_2 ...
>
> In order to remove this indefiniteness in the conception of peroxides, I propose to call peroxides only those oxides which are able to give hydrogen peroxide. If water is considered as the type of acids and bases, then hydrogen peroxide is the type of peroxides ... If water is considered to correspond to ordinary oxygen, peroxides should be linked with ozone. Oxides should therefore be separated into two series:
>
> 1) Saline oxides, able to give salts (acids, alkalis, etc.), like H_2O { basic, e.g. Na_2O, BaO; intermediate - Al_2O_3, PbO_2; acidic - CO_2, SO_3
>
> 2) Peroxides do not give salts, like hydrogen peroxide, e.g. Na_2O_2, BaO_2, KO_2.[59]

Continuing in the same paper, Mendeleev again pointed to the correspondence between the arrangement of the groups in the short-form periodic table and the value of the highest valency shown by the elements in their saline oxides:

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[57] PLBA, 51, 53. For further remarks made by Mendeleev in the same paper concerning the characterisation of the groups of the periodic table by means of the forms of their highest "saline" oxides, see Ch.III, p.186.

[58] J.Russ.Chem.Soc., 3 (1871) 284-6 (PLBA, 177-81).

[59] Op.cit., pp.284-5 (PLBA, 177-8).

> It is necessary to have in view the separation of the oxides into peroxides and saline oxides when applying the law of periodicity to the determination of the composition of the highest oxides. Only saline oxides are encountered in all of the groups, and only for them is it correct that the elements, arranged in the order of increasing atomic weight, give recurring series of highest oxides of composition R_2O, R_2O_2, R_2O_3, R_2O_4, R_2O_5, R_2O_6, R_2O_7, R_2O_8; the true peroxides do not enter into these series - they are met with only in the first groups, the saline oxides of which have a distinctly basic character.[60]

Mendeleev's distinction between "saline oxides" and "peroxides" was maintained by him throughout his life, as was his recognition of correspondence between group-number in the periodic table and the value of the highest valency shown by the elements of the group in their saline oxides. For example, in his Faraday Lecture (1889) he wrote:

> Those higher oxides which give salts - the formation of which oxides is foreseen by the periodic system, for example for the small period beginning with sodium, Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl_2O_7 - must be clearly distinguished from the still higher degrees of oxidation which correspond to hydrogen peroxide and possess the character of true peroxides ... such as Na_2O_2, BaO_2 ... In the properties of all such peroxide compounds there are a number of clearly evident common characteristics which distinguish them from the actual higher salt-forming oxides, especially their ease of decomposition with the help of certain contact agents, their incapacity for forming salts of the usual kind, and their tendence to combine with other peroxides (corresponding to the tendency of hydrogen peroxide to combine with barium peroxide ...).[61]

Mendeleev's characterisation of the groups of the periodic table in terms of the forms of what he called the "highest saline oxides" of the elements was criticised by Wyrouboff in 1896 as involving an "arbitrary selection of oxides";[62] earlier, in 1885, Ostwald had written, "the oxidation steps held up by Mendelêeff as characteristic or typical are

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[60] Op.cit., 285 (PLBA, 178). More than 30 years later, in the 7th (1902-3) and 8th (1906) editions of Pr.Ch., Mendeleev had the following to say on the question of the systematisation of the peroxides: "There is no doubt that similar elements very often give also similar peroxides, and the study of the peroxides - as the investigations of Piccini, Melikov, Pisarzhevskii and others have shown - consolidates the periodic system of the elements. But the subject still has incomplete factual material, and few direct relations to the fundamental properties of the elements, and therefore a general system of the peroxides is, in my opinion, a matter for the future" (e.g. Pr.Ch., R-8, 1906, n.403; PLBA, 313).

[61] PLBA, 232-3.

[62] See Chem. News, 74 (1896) 31.

neither the only ones, nor the lowest, nor yet the highest, indeed they are often unknown and incapable of existence".[63] These criticisms were largely unjustified, and reflected a lack of appreciation on the part of Ostwald and Wyrouboff of the particular significance attached by Mendeleev to these oxide-forms, viz. that they represented the highest "saline", or "non-peroxide", oxides characteristic of the group. Nevertheless, such criticisms were not completely without foundation. Ostwald's remark that Mendeleev's characteristic oxide-forms "are often unknown" was certainly true for the cases of O, F and most of the elements of group VIII: the absence of the compounds OO_3 (i.e. O_4) and F_2O_7 was explained by Mendeleev himself as being an example of the peculiarities often shown by the so-called "typical" elements;[64] the occurrence of the form MO_4 for only two of the group-VIII elements (viz. Ru and Os) was noted by Mendeleev, who in 1871 suggested tentatively, "Ferric acid will probably give FeO_4?".[65] Another defect in Mendeleev's particular characterisation of the groups in terms of their "highest saline oxides" concerns the oxide CuO. Copper was included by Mendeleev as an analogue of Na in group I[66] (the form of "highest saline oxide" of this group being listed as R^2O), and yet it gives the oxide CuO which, as acknowledged by Mendeleev himself, "forms salts, and does not give hydrogen peroxide, and therefore cannot be included among the true peroxides".[67] This and related but lesser anomalies arising in connection with the oxides of the other coinage metals were taken by Mendeleev to show that "the division of oxides into saline oxides and peroxides should not be taken as absolutely sharp",[68] and were seen by him as a reflection of the fact that the coinage metals show an analogy not only to Na but also to the elements

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[63] Lehrbuch der Allgemeinen Chemie, 1885, pp.126-7. The English translation given here is from Venable, Bibl.124, pp.115-7.

[64] A natural system of the elements (R.), 1870, p.42 (PLBA, 87).

[65] The periodic lawfulness of the chemical elements (G.), 1871, p.147 (PLBA, 113). This prediction has not been fulfilled; the highest known oxidation state for Fe is VI, in the ferrate ion FeO_4^{2-}.

[66] In Mendeleev's short-form tables published from 1871 onwards, Cu was included both in group I and in group VIII, as also were Ag and Au (see below, n.69).

[67] A note on peroxides (R.), 1871, p.286 (PLBA, 181).

[68] Ibid., p.285 (PLBA, 180).

of group VIII such as Ni and Pd.[69]

The mode of incorporation of the inert gases into the periodic table in 1900 seemed to provide strong support for Mendeleev's identification of group-number with the value of maximum saline valency: here was a case of a family of elements which apparently lacked the capacity for forming saline compounds (i.e. whose maximum saline valency was apparently = 0), and which fitted naturally into the periodic table as a new group preceding group I (i.e. as a new group whose group-number = 0).[70]

Mendeleev's identification of group-number in the periodic table with the value of the highest valency shown by the elements of the group in their "saline oxides" represented a significant contribution to the development of the notion of valency. With the emergence of the theory of the electronic structure of the chemical atom, the tendency of the elements to show a maximum positive valency (what Mendeleev referred to as maximum valency in "saline oxides") corresponding in value to group-number in the periodic table came to be explained in terms of the particular electronic configurations of the atoms, by the tendency to attain the stable "closed-shell" electronic configurations of the inert-gas atoms by means of the loss or sharing of electrons in chemical combination (Kossel, Lewis, 1916[71]).

In addition to relating the 8 forms of highest saline oxide to the 8 groups of his periodic table, Mendeleev also considered the relationship between degree of acidity or basicity of the saline oxides and position of the elements in the periodic system. Typical of his comments on this subject are the following, from the 3rd (1877) edition of Principles of Chemistry:

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[69] See, for example, The periodic lawfulness of the chemical elements (G.), 1871, pp.154-5 (PLBA, 118-9). This double analogy shown by the coinage metals - on the one hand to Na, on the other hand to Ni, Pd and Pt - was reflected in all Mendeleev's published short-form tables from table 30 (P7) (1871) onwards in the inclusion of these elements in both group I and group VIII: one set of entries was usually enclosed in parentheses, this tending to be the group-I entry in the tables of the 19th century, and group-VIII entry in the 20th-century tables. In Mendeleev's long-form tables the coinage metals were listed only once, as analogues of Na in group I - see, for example, tables 32 (1871), 52 (1889) and 63 (1906).

[70] See Ch.VII, section C, where Mendeleev's views concerning the inert gases are considered in detail.

[71] W. Kossel, Ann.Physik, [4], 49 (1916) 229. G.N. Lewis, J.Amer. Chem.Soc., 38 (1916) 762.

> The oxides of the even series generally possess more strongly basic properties than the oxides of the same type of composition in the odd series; the latter are endowed mainly with acidic properties. Furthermore, acidic character is shown primarily by the lightest elements, and basic properties by the heaviest. Thus, among the lightest (the typical) elements predominate those which give acids, especially in the later groups; and the heaviest elements - even in the later groups (e.g. Th, U) - have a basic character. The basic and acidic characters of the highest oxides are determined, therefore, by: a) the form of the oxide [sc. by the group, since the form of the highest oxide is characteristic of the group], b) the even or odd series in which the element is found, and c) the magnitude of its atom. For the lower oxides the character is determined by the form of the oxide and by the properties of the highest oxide. Thus, the oxide of arsenic (gr.V, series 5) As_2O_5 is distinctly acidic, but in As_2O_3 the acidic properties are less developed.[72]

Just as Mendeleev distinguished two kinds of oxide (viz. saline oxides and peroxides), he distinguished also two kinds of hydride - the usual volatile hydrides, formed by the heavier elements of the Li - F series and of the odd series in the short-form periodic table, and the non-volatile hydrides, formed by certain elements of the even series (excluding the Li - F series), e.g. K, Ba, Pd.[73] Mendeleev's distinction between volatile and non-volatile

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[72] Pr.Ch., R-3 (1877) 849 (PLSM, 351).

[73] From 1871 the Li - F series was designated "series 2" by Mendeleev, i.e. it was an "even" series (see Ch.III, p.190). However, in many respects - the formation of volatile hydrides being one, the formation of volatile organo-compounds (see later) being another - this series resembles the "odd" series. On this matter Mendeleev wrote (Annalen, 1871, pp.153-4; PLBA,117): "It appears that the justification of the division into even and odd series is violated by the second series - Li, Be, B, C, N, O, F, because the members of this even series possess acidic properties, [and] form both hydrides and organometallic compounds ..., i.e. they resemble the elements of the odd series. But in relation to this series it should be noted: 1) that, unlike other even series, it is not followed by the VIIIth group, 2) that the atomic weights of its members differ from the atomic weights of the corresponding members of the next series by about 16, whereas between all later series this difference is 20 - 28. The elements of all other even series differ in atomic weight from the elements of the nearest even series by about 46, but these elements of the 2nd series differ from the elements of the 4th by only 32 - 36 ... This elucidates the seeming deviation, and even supports our main position - the dependence of the change of properties upon change of atomic weight. Here we have a change in magnitude of atomic weight different from in the other series, and therefore the relationship of properties is also different."

hydrides seems to have been first made in late 1870: in his article A natural system of the elements (R.), written in Nov.-Dec. 1870, he referred to the tendency of certain of the elements of group VIII (which occupy even series in the short-form periodic table), such as Cu[74] and Pd, to give "unstable compounds with hydrogen ... which do not resemble the usual hydrides - they are involatile, easily decomposed, and not one of them has yet been obtained in the form of a substance of completely definite composition".[75] In 1877, in the 3rd edition of Principles of Chemistry, Mendeleev wrote: "Hydrides, as volatile or gaseous substances of distinctive reactions, such as HCl, H_2O, H_3N and H_4C, are formed only by elements of the odd series and the higher groups which give oxides of composition R_2O_7, RO_3, R_2O_5 and RO_2. If the elements of the even series give hydrides, then these - such as K_2H - are easily decomposed, are involatile, and possess a completely different character (metallic) from the usual hydrides".[76] In the corresponding passage from the 8th (1906) edition of Principles of Chemistry we find the remarks:

> Hydrides, as volatile or gaseous substances of distinctive reactions, such as HCl, H_2O, H_3N and H_4C [408], are formed only by elements of the odd series and the higher groups which give oxides of composition R_2O_7, RO_3, R_2O_5 and RO_2.
>
> .....
>
> [408] The hydrides which are generalised by the periodic law are ... volatile or gaseous. Hydrides such as NaH, BaH_2, etc. are distinguished by other characteristics. They show ... a systematic harmony, but they evidently should not be confused with the usual hydrides, any more than peroxides with saline oxides. Moreover, such hydrides, like the peroxides, have only recently begun to be studied, and have been investigated but little.[77]

As regards the trends in the properties of the volatile hydrides in passing along a row in the vertical short-form periodic table, Mendeleev wrote in 1871:

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[74] Cu was included by Mendeleev also in group I of the short-form periodic table, in which case it occupies an odd series, viz. series 5 (see n.69, above).

[75] Op.cit., pp.42-3 (PLBA, 87-8).

[76] Pr.Ch., R-3 (1877) 849 (PLSM, 351).

[77] Pr.Ch., R-8 (1906) 256, 617 (PLBA, 292, 322). In the corresponding passage from R-7 (1902-3) Mendeleev gave the formula for sodium hydride as Na_2H (cf. K_2H in the passage from R-3, 1877, quoted above) rather than NaH. Before ca.1900 the formula-type M_2H was fairly generally adopted for the hydrides of Na and K, on the basis of the work of Troost and Hautefeuille (1870's). The correct formula-type MH was indicated by the investigations of Moissan (ca. 1900).

> The stability or decomposability of these hydrides under various influences, their acidic properties - or the tendency for their hydrogen to be substituted by metals - and other such properties, change gradually and regularly according to the relative position of the elements in the rows. Thus HCl is a distinct acid, of great stability; H_2S is already a weak acid, decomposed by heat; in H_3P there are already no acidic properties, and the decomposability has increased - and these characteristics are even more distinct in H_4Si.[78]

The relationship between the forms of composition of the volatile hydrides and the highest saline oxides of the elements was first discussed by Mendeleev in 1869, in his paper On the quantity of oxygen (R., publ. 1870):

> If we apply the above system [sc. table 13 (P4)] of the elements to the comparison of their hydrogen compounds, then we find for these latter a sequence opposite to that which exists for the oxygen compounds. The halogens combine with one equivalent of hydrogen; oxygen, sulphur and analogues, with 2 equivalents of hydrogen; nitrogen, phosphorus, etc., with 3; carbon, silicon, with 4; for the first 3 groups hydrogen compounds are not at present known. By analogy we may judge that boron and aluminium are able to form, as their highest stage of combination with hydrogen, BH_5 and AlH_5.[79]

By early 1871 Mendeleev had come to discard the hypothesis that the elements of group III form hydrides RH_5. He now began to draw attention to the empirical result - which we shall call his "rule-of-4"[80] - that the maximum number of hydrogen or oxygen atoms which can combine with a single atom of some other element to form a volatile hydride or saline oxide is 4, and that the maximum number of oxygen atoms combined with one atom of another element in an acidic hydrated saline oxide (what Mendeleev referred to as an "acidic hydrate") is also 4. Thus, in part II of the 1st edition of Principles of Chemistry (publ. March 1871) he wrote:

> Returning to the form RO_4, we pay heed to the fact that RH_4 is the highest of the known forms of hydrogen compound, and that the highest forms of acidic hydrates - SiH_4O_4, PH_3O_4, SH_2O_4, $ClHO_4$ - all contain four atoms of oxygen; and therefore in this number [sc. in the number 4] there is, evidently, a limit for the simplest forms of compounds of hydrogen and oxygen. To a few atoms of an element or elements there may be attached more than O_4, H_4, but to a single atom in a molecule this is never the case. Thus, the simplest forms of the compounds of hydrogen and oxygen are exhausted by - RH_4, RH_3, RH_2, RH, RO, RO_2, RO_3, RO_4. The limiting cases RH_4 and RO_4, we note,

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[78] Annalen, 1871, p.141 (PLBA, 108).

[79] Op.cit., p.19 (PLBA, 55).

[80] The term "rule-of-4" is used here for the sake of terminological harmony with the so-called "rule-of-8" (see below).

are found only for bodies, such as C, Si, Os and Ru, which also give, with chlorine, RCl_4. This numerical collation does not agree with the usual form of collation, because equivalence exists between H_2-Cl_2-O, and not between H-Cl-O, but it is worthy of attention because of its simplicity. The collation or confrontation of RH_4 with RO_4 is demanded not only by the fact that in these limiting forms exist the least stable bodies (we compare SiH_4, PH_3, SH_2, ClH, or RuO_4, MoO_3, ZrO_2, SrO), which readily give off part or even all of the O or H combined with them, but also by the fact that of all the elements those which give the forms RH_4 and RO_4 are the most physically-alike, the least active in the free state, having extremely small atomic volumes (C = 4.5, Si = 11, Ru = 9, Os = 9.5), and again because the equivalence of O and H_2 corresponds to one form, H_2O, of combination of H with O, and the correspondence of H and O to the other form, H_2O_2.[81]

This "rule-of-4" was again stated by Mendeleev later in 1871, in his article on The periodic lawfulness of the chemical elements (G.).[82] Here we also find an explicit recognition of the relation which is now sometimes known as the "rule-of-8",[83] that the sum of the maximum valencies of an element with respect to O in saline oxides and H in volatile hydrides is equal to 8 (this "rule-of-8" had already been implicit in the above-quoted comments of 1869 from Mendeleev's On the quantity of oxygen):

> The sum of the equivalents of hydrogen and oxygen which are conjoined separately to one atom of an element does not exceed 8; and therefore the elements giving RO_4 do not form hydrogen compounds. Those which can give R_2O_7, form RH; those which give RO_3, form RH_2; those which give R_2O_5, form RH_3; and those which give RO_2, form RH_4. Those elements which with oxygen give a highest form R_2O_3, have not as yet given hydrogen compounds, because the complementary hydride form RH_5 does not exist.[84]

Mendeleev was the first to point to the "rule-of-8" relation. His contribution in this respect is rarely recognised, however, priority in drawing attention to this relation usually being attributed to Abegg (1904).[85]

In the 3rd (1877) and later editions of Principles of Chemistry Mendeleev linked the "rule-of-4" (as applied to "acidic hydrates") with the "rule-of-8", in terms of the further generalisation that "the quantity of hydrogen in a hydrate equals the content of hydrogen in the hydride":

> ... the acidic hydrates and their salts, with a single atom of an element, contain in all the highest forms not more than four atoms of oxygen, just like the highest saline form RO_4 ... The hydrate of the oxide RO_2 in the highest form is $RO_2{\cdot}2H_2O = RH_4O_4 = R(HO)_4$ ... The oxide R_2O_5 corresponds to the hydrate $R_2O_5{\cdot}3H_2O = 2RH_3O_4 = 2RO(OH)_3$)... The hydrate of the oxide RO_3 is $RO_3H_2O = RH_2O_4 = RO_2(OH)_2$ ... The hydrate

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[81] Pr.Ch., R-1, part II (1871) 835 (PLBA, 382).

[82] Op.cit., p.142.

[83] The term "rule-of-eight" is used, for example, by T. Moeller in his Inorganic Chemistry, an advanced textbook, New York (John Wiley) and London (Chapman and Hall), 1952 (6th printing 1957), Ch. 6.

[84] Op.cit., p.225 (PLBA,172). The last statement in this passage, that "RH_5 does not exist", seems to have been made as a deduction from the "rule-of-4" rather than merely as an isolated statement of non-observation.

[85] R.Abegg, Z. anorg.Chem., 39 (1904) 330.

> corresponding to R_2O_7 is, evidently, $RHO_4 = RO_3(OH)$ ... Here, besides the content O_4, it must further be noted that the quantity of hydrogen in a hydrate equals the content of hydrogen in the hydride. Thus, silicon gives SiH_4 and SiH_4O_4, phosphorus PH_3 and PH_3O_4, sulphur SH_2 and SH_2O_4, chlorine ClH and $ClHO_4$. This circumstance at least brings into a harmonious system the fact that the elements which can combine with a greater amount of oxygen are able to retain less hydrogen, even if it does not explain this fact ... The sum of the equivalents of hydrogen and oxygen which are found in combination with an atom of nitrogen in the highest forms, equals eight. So also for the other elements which combine with oxygen and hydrogen.[86]

Mendeleev was one of the first to use the hydroxyl (OH) notation for the "acidic hydrates" which is employed by him in this passage.[87] His earliest use of this notation seems to have been in the article On the place of cerium (G.), published in 1871.[88]

Mendeleev's two London lectures of 1889 - viz. his Royal Institution lecture (May 31st) and his Faraday lecture (June 4th) - are both of interest in connection with his "rule-of-4" and "rule-of-8". In his Faraday lecture Mendeleev states these rules as follows: "Not more than 4 atoms of hydrogen or oxygen are joined to a single atom of an element ... The periodic law has shown ... that the capacity for combination of the non-metals with oxygen is directly determined by their capacity to combine with hydrogen, and the sum of the equivalents of both is for all elements = 8".[89] In his Royal Institution lecture Mendeleev implies some special universal significance for the numbers 4 and 8:

> Because more than four atoms of hydrogen do not combine with one atom of an element; because the hydrogen compounds (e.g. HCl, H_2S, H_3P, H_4Si) of the elements form higher acids always with 4 atoms of oxygen; because the highest known form of the oxides (OsO_4 and RuO_4) contains also 4 oxygens; because the eight groups of the periodic system, corresponding to the highest saline oxides, R_2O, RO, R_2O_3, R_2O_5, RO_3, R_2O_7 and RO_4, imply the relationships mentioned; and because, of the closest analogues among the elements (as, for example, Mg, Zn, Cd and Hg; or Cr, Mo, W and U; or Si, Ge, Sn and Pb; or F, Cl, Br and I; etc.), more than 4 is unknown - then it seems to me that these relations are of profound interest and significance for chemical mechanics. And because the idea of unity in the plan of nature, acting in the composition of heavenly systems and chemical molecules, seems a very attractive idea to my imagination, especially because then the atomic doctrine immediately acquires its true significance, I shall recall the following facts relating to the solar system: there are 8 major planets; of these, the 4 inner ones are not only separated by the asteroids from the 4 outer ones, but also differ from them in many respects (e.g. having small diameters and high density); Saturn, with its ring, has 8 satellites, and Jupiter and Uranus have 4 each. From this it is evident that in the solar system we meet those same numbers, 4 and 8, which appear in connection with the composition of the chemical molecules.[90]

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[86] Pr.Ch., R-3 (1877) 844-5 (PLSM, 346).

[87] This has been pointed out by A. Wurtz, Bibl.133, p.174.

[88] Op.Cit., p.48 (PLBA,64): "$CeH_2O_3 = CeO(OH)_2$".

[89] PLBA, 231-2.

[90] PLBA, 544, footnote.

2. The relationship between the position of an element in the periodic system and its faculty for forming organometallic compounds.[91]

Mendeleev was well acquainted with the preparation and properties of various organometallic compounds at least eight years before his discovery of the periodic law, having discussed this subject in his textbook on Organic Chemistry (R.), 1861.[92] The earliest known record of his interest in the relationship between the position of an element in the periodic system and its faculty for forming organometallic compounds is that provided by table 24 (M17) (a), dated 17th November (O.S.) 1870.[93] This manuscript was written mainly in ink, but in the right-hand margin and also next to certain places within the table the values of the boiling-points and specific gravities of various ethyl compounds are given in pencil; and at the foot of the table is written, also in pencil -

Metallo-org
only unev
Of the even?

The expanded version of this comment would presumably be something like, "Metallo-org[anic compounds have been obtained] only [for metals of the] unev[en series. What about the metals] of the even [series]?".[94] That metals of the uneven (odd) series form organo-compounds whereas metals of the even series do not was pointed out by Mendeleev shortly afterwards in his article A natural system of the elements (R.; dated 29th Nov., O.S., 1870):

> ... the metals of the even series are characterised ... by the fact that for them not a single organometallic (metalloorganicheskogo) compound is known ..., whereas organometallic compounds are known for almost all of the elements which are placed in the odd series. In the first series [sc. "series 1" according to Mendeleev's earlier (incomplete) system of numeration of the series (see Ch.III, pp.189-90): Na, Mg ... Cl] such compounds are known for magnesium, for aluminium, and for silicon, phosphorus, sulphur and chlorine, whereas for the elements of the 2nd series [sc. K, Ca, Ti, etc.] not a single organometallic compound has yet been obtained. The attempts of Cahours and Buckton to prepare titanoethyl compounds were, as is well-known, completely

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[91] On this subject see Kedrov's account of The location of elemento-organic compounds in the short table (R.), Sc.Ar., 839-45.

[92] The first organometallic compound to be discovered was tellurium diethyl, $TeEt_2$, obtained by Wöhler in 1840. In 1849 Frankland prepared zinc methyl and zinc ethyl, $ZnMe_2$ and $ZnEt_2$. During the 1850's and early 1860's a number of other organometallic compounds were discovered, as also were compounds of semi-metals with alkyl radicals, e.g. BEt_3.

[93] A commentary by Kedrov on the composition and content of this manuscript, table 24 (M17) (a), is given in Sc.Ar., 172.

[94] A similar expansion of Mendeleev's abbreviated note is suggested by Kedrov, Sc.Ar., 159 and 840.

> unsuccessful; although the chlorides of silicon and titanium resemble each other so closely in their formulae, in their reaction with water, and also in a multitude of other properties, they are sharply distinguished in their reactions with zinc ethyl, viz. silicon chloride readily gives silicon ethyl, whereas titanium chloride does not enter into such double decomposition. This difference extends as far as the very last members, viz. in the 9th series mercury, lead and bismuth have given organometallic compounds. For thallium, at least an ether compound, corresponding to its lower degree of oxidation, is known; and we may consider that neither uranium, tantalum nor tungsten, nor also cerium, zirconium and molybdenum, will give organometallic compounds, just as titanium does not form them. On the other hand, indium and thallium, belonging to the odd series, will certainly give organometallic compounds $InEt_3$, $TlEt_3$, the study of which should be of interest for resolving the uncertainty regarding the formula of aluminium ethyl.[95]

Similar remarks are to be found in Mendeleev's 1871 article on The periodic lawfulness of the chemical elements (G.).[96] But since Mendeleev in this paper had extended the numeration of the series to include the "typical" elements H and Li - F he was now confronted with the anomaly of the formation of organo-compounds by the elements of an "even" series (viz. "series 2", Li - F, giving BEt_3, CEt_4, NEt_3, OEt_2, EtF). His explanation of this anomaly (and of other anomalous properties of the "typical" elements Li - F) was in terms of the atomic-weight differences between the series of the short-form periodic table (see n.73 of the present chapter).

In the 3rd (1877) edition of Principles of Chemistry Mendeleev had the following to say about the relationship between the position of an element in the periodic system and its faculty for forming organometallic compounds:

> If an element gives a hydride RX_n, then it will form an organometallic compound of the same composition, where $X = C_nH_{2n+1}$, i.e. X is the residue of a saturated hydrocarbon. The elements of the odd series which are not able to give hydrogen compounds and which give oxides of the form RX, RX_2, RX_3 also give organometallic compounds, of the form characteristic of the highest oxides. Thus, zinc forms an oxide ZnO, salts ZnX_2, and zinc ethyl $Zn(C_2H_5)_2$. The elements of the even series seem not to give organometallic compounds at all - at least, all efforts to obtain them have so far been in vain, e.g. for titanium, zirconium and iron.[97]

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[95] Op.cit., p.34 (PLBA, 78-9). The compounds $InEt_3$ and $TlEt_3$ predicted by Mendeleev in the last sentence of this passage did indeed turn out to exist. The "uncertainty" to which he refers here in connection with aluminium ethyl was whether the formula is $AlEt_3$ or Al_2Et_6. (Cryoscopic studies of aluminium ethyl in ethylene dibromide by Louise and Roux in 1888 indicated the dimeric form, Al_2Et_6; the presence of the dimeric form has been subsequently shown also by vapour-density measurements. The indium and thallium ethyls on the other hand are monomeric, $InEt_3$ and $TlEt_3$).

[96] Op.cit., pp.152-3 (PLBA, 115,117).

[97] Pr.Ch., R-3 (1877) 849 (PLSM, 351).

In the corresponding passage of the 7th (1902-3) edition of Principles of Chemistry the last sentence has become, "The elements of the even series (large periods) form organometallic compounds with difficulty";[98] and in the 8th (1906) edition the corresponding sentence is omitted from the passage.[99] By the early 20th century, therefore, Mendeleev's distinction between the elements of the even (excluding Li - F) and odd series as regards tendency to form organometallic compounds appears to have become somewhat less strict than previously. The specific reasons for this were not given by Mendeleev.

3. Horizontal, vertical and diagonal relationships in the short-form periodic table.[100]

From the outset of his work on the periodicity of properties of the elements Mendeleev was necessarily concerned with the vertical and horizontal relationships in the periodic table, since it is these very relationships - within the groups, periods and series - which are directly expressed in the periodic law. Similarly, insofar as he tended to present the periodic table in the zig-zag short-form arrangement (which he commonly did from early 1871 onwards) Mendeleev was also very much concerned with what might be considered to be a certain type of "diagonal" relationship, viz. the relationship between the elements of the different sub-groups of a given group, which in the zig-zag short-form table is "diagonal" because of the zig-zag arrangement of the elements within the groups. Those relationships to which the term "diagonal" is more usually applied, between elements which occupy not only different series or periods but also different groups (not merely different sub-groups of the same group), were of much lesser concern to Mendeleev.

As regards Mendeleev's consideration of the vertical and horizontal relationships within the periodic table, on the question of the vertical and horizontal analogies of the elements he wrote in November 1870, in reference to the vertical short-form arrangement of the elements which was published as table 33 (P10), "The main thing that I wish clearly to display consists in the fact that resemblance exists along both the vertical and the horizontal rows. Thus, according to the properties of its compounds, Nb shows

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[98] Pr.Ch., E-3 (1905; from R-7, 1902-3) II, 25.

[99] See Pr.Ch., R-8 (1906) 256 (PLBA, 292).

[100] See Kedrov, Sc.Ar., 817-22: The revealing of the main and secondary trends in the short table (R.).

resemblance both to V and Ta, and to Zr and Mo".[101] In a passage written shortly afterwards, in the article A natural system of the elements (R.), Mendeleev introduced the term "atomanalogy" in connection with the horizontal and vertical analogies of the elements in the zig-zag short-form periodic table:

> ... for each element its resemblance to other elements is expressed in its place in the horizontal and vertical rows. I propose to call this double resemblance of the elements their atomanalogy (atomanalogieiu). Thus, zirconium is an atomanalogue of Ti, Ce, Th, because it is found in the same vertical row, and shows much similarity to them; and also of Sr, (Yt?), Nb, Mo, because it has an atomic weight close to theirs in value, and its compounds have similar properties to theirs. Elements which are found together in nature (prirodnye sputniki) are usually atomanalogues.[102]

Later in the same article Mendeleev uses the shorter terms "atomology" and "atomologue" for "atomanalogy" and "atomanalogue". In his article on The periodic lawfulness of the chemical elements (G.), published in November 1871, Mendeleev came to restrict his use of the term "atomanalogy" (or "atomology") to the designation of the resemblance of an element to its nearest vertical (same sub-group) and horizontal (same series) neighbours only:

> The position of an element R in the system is defined by the series and by the group to which it belongs - or by the elements X and Y standing next to it in the same series and the elements R′ (with smaller atomic weight) and R″ (with larger atomic weight) standing next to it in the same group.[103] Knowing the properties of X, Y, R′, R″, the properties of R are defined. We thus have the following series in the system:
>
> series (n - 2) X′R′Y′
>
> series n X R Y (R″ - R is approximately = R - R′ = about 45).
>
> series (n + 2) X″R″Y″
>
> ... The relationship of R to X and Y on the one hand, and to R′ and R″ on the other, I call the atomanalogy of an element. Thus the atomanalogues of Se are As and Br on the one hand, and S and Te on the other. Its atomic weight is the mean, $\frac{75 + 80 + 32 + 125}{4} = 78$; so also the properties of SeH_2 are the mean of the properties of AsH_3 - BrH and SH_2 - TeH_2, and so on. Only in the extreme rows

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[101] On the place of cerium (G.), publ. 1871, p.451 (PLBA, 65).

[102] Op.cit., p.43 (PLBA, 88).

[103] It is clear from what follows in this passage that by "same group" Mendeleev here actually means "same sub-group".

> and groups is it impossible to apply these atomological relationships completely, but here also we can observe clear correlations, which I shall express provisionally by proportions (arithmetical, not geometrical, proportions); thus, $X' : X = R' : R = Y' : Y$, or $X' : R' = X : R = X'' : R''$, etc.[104]

First in the article A natural system of the elements (R., 1871), and then in The periodic lawfulness of the chemical elements (G., 1871), Mendeleev made extensive use of the "atomanalogical" relationship as a basis for interpolation and extrapolation of the periodic system (see Ch.VI). After 1871 he continued to point to this relationship and its applicability to prediction, and to base predictions upon it, but he now no longer employed the terms "atomanalogy" (or "atomology"), "atomanalogical" ("atomological") and "atomanalogue" ("atomologue").[105]

An interest in "diagonal" relationships in the short-form periodic table, beyond merely those relationships between the elements of the different sub-groups of the same group in a zig-zag arrangement, was shown by Mendeleev in two manuscripts dating from 1870, viz. table 16 (M10) (a) and table 24 (M17) (a). In these two manuscript short-form tables Mendeleev had drawn lines linking the elements in diagonal directions, and had marked in the atomic-weight differences between adjacent elements along these diagonals; in table 24 (M17) (a) he gave also the overall atomic-weight differences for some of the longest diagonal series. The diagonal connections considered by Mendeleev in tables 16 (M10) (a) and 24 (M17) (a) are shown, in isolation from the additional content of these tables, in Figs. V-3 and V-4 respectively (see below). Although table 16 (M10)(a) is in fact a horizontal table, Fig. V-3 is given in vertical form for convenience of comparison with Fig. V-4. Because table 16 (Fig. V-3) has a partially zig-zag arrangement whereas table 24 (Fig. V-4) has a full zig-zag arrangement, the particular diagonal series marked in these two tables differ in the connections of the Li - F row to the Na - Cl row.

Mendeleev did not publish any study of diagonal atomic-weight relationships corresponding to that indicated in the manuscript tables 16 (M10)(a) and 24 (M17)(a). His published remarks on diagonal relationships other than merely the zig-zag relationship within the groups in the zig-zag

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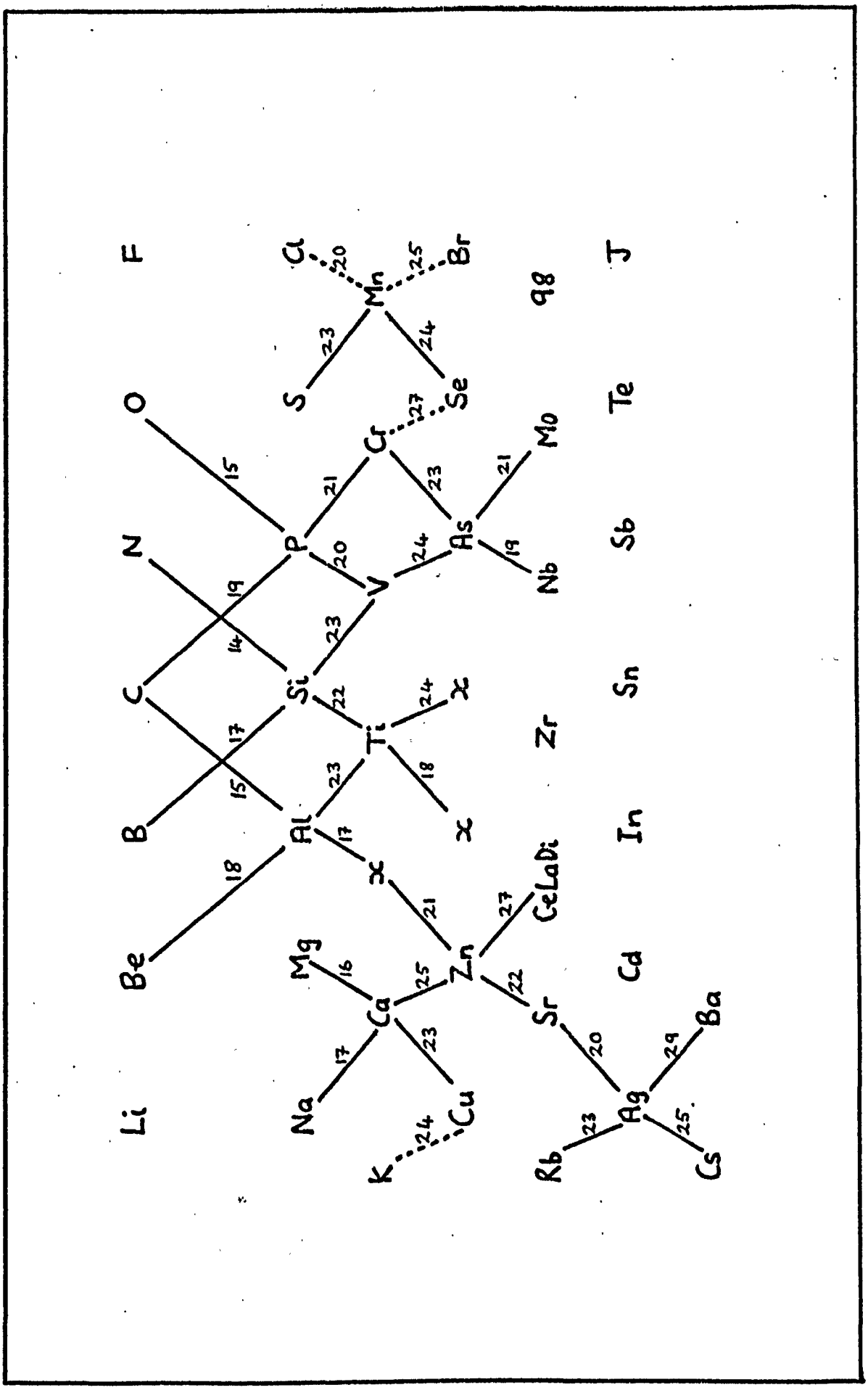
[104] Op.cit., pp.164-5 (PLBA, 126-7).

[105] See, for example, Pr.Ch., R-3 (1877) 850 (PLSM, 352-3; R-8 (1906) 256-7 (PLBA, 293-5).


F
O
N
C
B
Be
Li
Cl
Mn
Br
S
Se
Cr
Mo
P
As
V
Nb
Si
Ti
Zr
Al
In
Mg
Ca
Zn
Cd
Na
Cu
Sr
Ba
K
Ag
Rb
Cs
J
Te
Sb
Sn
98
CeLaDi
15
20
25
23
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16
29

Fig.V-3.

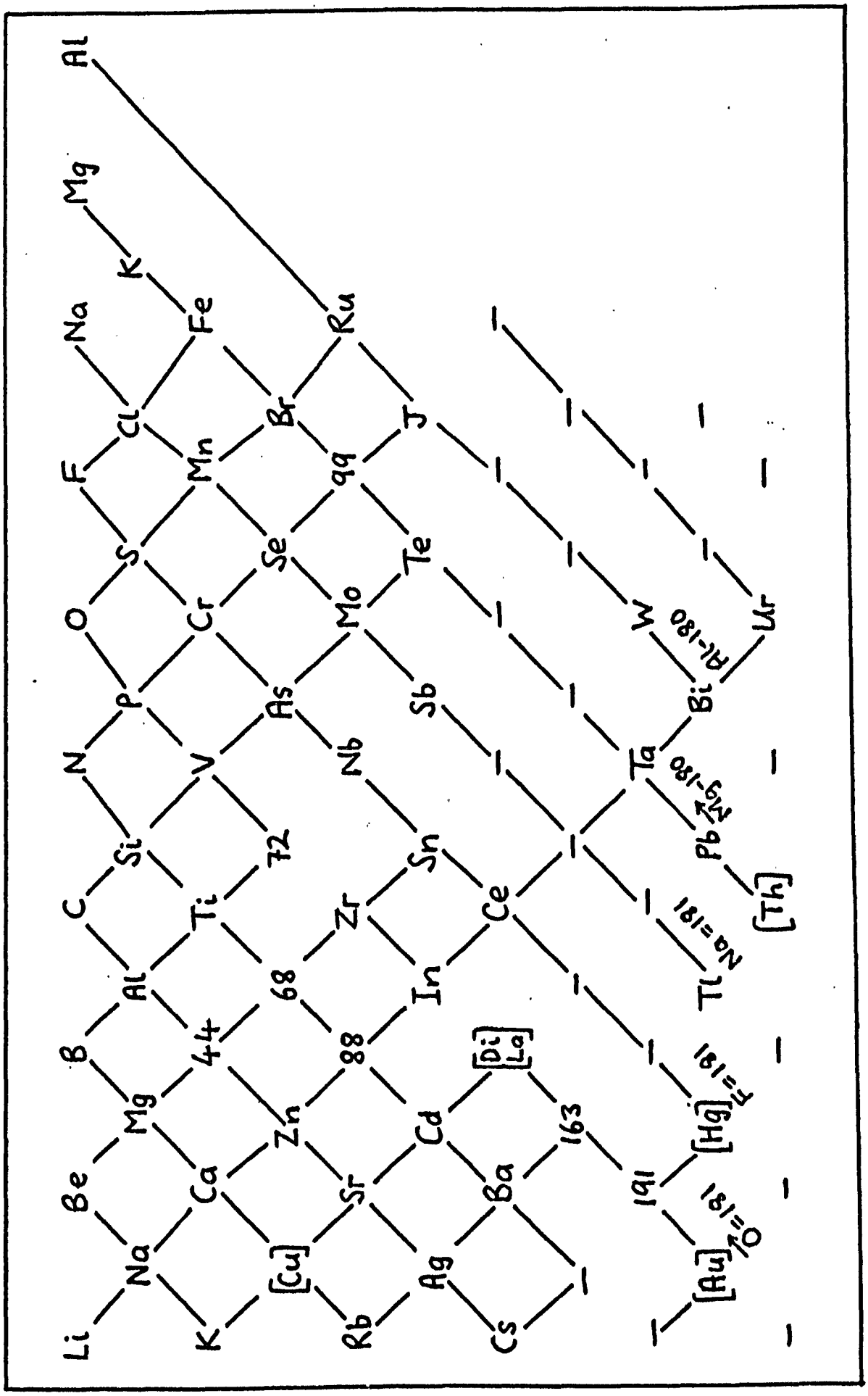
Al
Mg
K
Na
Fe
Ru
Cl
Br
J
F
Mn
99
S
Se
Te
O
Cr
Mo
W
Ur
P
As
Sb
Bi
Pb 207-180
N
V
Nb
Ta
Th
Si
72
Sn
C
Ti
Zr
Ce
181=Na
Al
68
In
Tl
B
44
88
[Di]
[La]
181=H
Mg
Zn
Cd
163
[Hg]
Be
Ca
Sr
Ba
191
181=O
[Au]
Na
[Cu]
Ag
Li
K
Rb
Cs

Fig.V-4.

short-form table concern certain diagonal analogies between elements of the Li - F row and elements of the Na - Cl row. Thus in his article The periodic lawfulness of the chemical elements (G., 1871), in the various editions of his Principles of Chemistry, and elsewhere, Mendeleev pointed to the existence of analogies between the elements in the following diagonally-related pairs: Li and Mg; Be and Al; B and Si; B and P; and C and S.[106] The first three of these pairs, but not the last two, correspond to diagonal connections which had been considered in Mendeleev's manuscript studies of 1870. The analogies between Li and Mg, between Be and Al, and between B and Si - particularly evident in the physical and chemical properties of the oxides and certain other compounds of these elements - were widely recognised.[107] The analogies which Mendeleev pointed out for the pairs B - P and C - S were less generally recognised: they consisted for B - P in the fact that B gives BCl_3, B_2O_3 and BH_3O_3, and P gives PCl_3, P_2O_3 and PH_3O_3, and for C - S in the fact that C gives CO_2, C_2H_2 and CH_2O_2, and S gives SO_2, S_2H_2 and SH_2O_2.

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[106] See especially The periodic lawfulness of the chemical elements (G.), 1871, pp.166-7 (PLBA,128).

[107] The analogy of Be to Al led a number of chemists to consider Be to be trivalent like Al rather than divalent like Mg. The controversy about the valency of Be, and consequently about whether its atomic weight is ca. 9 or ca. 14, persisted into the 1880's (see Ch.VI).

CHAPTER VI

MENDELEEV'S USE OF THE PERIODIC SYSTEM FOR THE DETERMINATION OF ATOMIC-WEIGHT VALUES AND FOR THE PREDICTION OF THE EXISTENCE AND PROPERTIES OF UNKNOWN ELEMENTS

A. Introduction

For Mendeleev the particular placing of an element in the periodic system had to fulfil simultaneously three types of requirement: the requirement of atomic-weight ordering; the requirements of family-resemblance; and the requirement of single-occupancy of places (with the exception of group VIII in the short-form table). The principle of atomic-weight ordering was allowed no exception by Mendeleev[1]; as regards the requirements of family-resemblance, chemical properties were taken as more significant than physical properties, the highest valency shown in "saline" ("non-peroxide") oxides being of fundamental significance. Any apparent discrepancy in the demands of atomic-weight ordering, family-resemblance and single-occupancy for the placing of a particular element was taken to indicate an error in the assumed atomic-weight value or family-resemblance - or perhaps both - of one or more of the elements involved. For example, most of the irregularities of atomic-weight ordering apparent in the final column of Mendeleev's original "attempt at a system", table 8 (P1), were shortly afterwards rectified by his moving of various elements in accordance with a re-assessment of family-resemblances without any alteration of atomic-weight values: thus, he came to take Hg (200) as being an analogue primarily of Zn and Cd rather than of Cu and Ag; Au (197) as more an analogue of Cu and Ag than of Al; Tl (204) as more an analogue of Al than of Na and K; and Pb (207) as more an analogue of Sn than of Ba; and these elements were accordingly re-positioned in his periodic table (see Ch.III, especially Fig. III-19, p.193). But more common than such re-positioning without atomic-weight modification, especially after mid-1869, was Mendeleev's positioning or re-positioning of elements in his periodic table with concomitant modification

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[1] There are two manuscript tables which were drawn up by Mendeleev where it might seem that he was contemplating allowing an exception to the principle of atomic-weight ordering, viz. table 6 (M6), where he suggests the atomic weight Nb = 97 (cf. Mo = 96), and table 24 (M17), where we appear to find the suggested atomic-weight value of 191 for an unknown element coming 3 places before Ta = 182. However, those suggestions seem rather to represent cases where Mendeleev had considered only a partial aspect of the atomic-weight trends in the periodic table, viz. only vertically, along the group N, P, V, As, Nb, Sb, in table 6, and only diagonally in table 24. There are no grounds whatever for thinking that he was prepared to persist in such suggestions when he saw that they violated the principle of atomic-weight ordering along the horizontal series of these tables; and indeed, these suggestions are to be found nowhere else in his work.

(or at least recognition of the need for modification) of the currently-adopted atomic-weight values.

In Mendeleev's use of the periodic system as grounds for modifying accepted atomic-weight values we can recognise two general types of such modification:-

i) Those cases where the recommended or adopted modification involved a change in the particular multiple employed for deriving the atomic weight from the empirically-determined equivalent, i.e. a change in the assumed valency, and hence in assumed family-resemblance: included in this category were Be, U, In, Th and certain rare-earth elements.[2]

ii) Those cases where what was involved was not a change in assumed valency, but merely the adoption or recommendation of a relatively slight adjustment in the atomic-weight value, corresponding to a slight adjustment in the value of the equivalent (implying a corresponding degree of error in the empirically-determined value of the latter): included in this category were U[3]; Ti; Te and I; Os, Ir, Pt and Au; Co and Ni; and Ar and K.[4]

Nearly all of these atomic-weight modifications were adopted or suggested by Mendeleev in response to apparent discrepancies in the demands of atomic-weight ordering, family-resemblance and single-occupancy (and in accordance with the demand that empty places in the periodic table be filled). Titanium, however, already had its own place in the periodic table, corresponding to the requirements both of atomic-weight ordering and family-resemblance, before Mendeleev changed its atomic weight. The adoption by Mendeleev of an atomic-weight value of 48 instead of 50 for titanium was based upon a desire for greater regularity in the atomic-weight differences in the row containing Ti in the short-form periodic table (i.e. the row K - Mn). The demand for regular atomic-weight differences was not one which Mendeleev usually made; normally he demanded no more regularity than conformity with the principle of atomic-weight ordering, as indicated for example in his comments of 1871 on "individual deviations" from strict regularity of atomic-weight differences in the sequence of elements arranged in the order of increasing atomic weight (see Ch. V, pp.296 - 7). His use of a

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[2] These cases, except for that of Be, are discussed by Kedrov in Sc.Ar., 799-817. Kedrov discusses the case of Be in Bibl.38, pp. 81-4.

[3] Mendeleev's type ii) modification for U was historically prior to his type i) modification for this element; it was rejected by him some months before he suggested the type i) modification (see later, section B).

[4] The atomic-weight values of certain rare-earth elements were also subjected to minor type ii) modifications after having been subjected to major type i) adjustments.

regular-spacing argument in the case of Ti seems to have been encouraged by the idea that the atomic-weight value of 50 obtained for this element might be too high because of "eka-silicon" impurity. Although this idea of the contamination of Ti by "eka-silicon" (= germanium) has turned out to be wrong, the atomic-weight value Ti = 48 was subsequently confirmed: however, as has already been noted by Koertge[5], this particular confirmation should be seen as no more than a fortuitous success of the periodic system. Similar to the case of Ti was the type ii) atomic-weight modification which Mendeleev made in 1871 for cerium, from Ce = 138 to Ce = 140.

Most of the atomic-weight changes associated with Mendeleev's adopting a different valency for an element turned out to be correct, whereas most of the changes demanded by his strict adherence to the principle of atomic-weight ordering were not vindicated, i.e.,of the various atomic-weight modifications adopted or suggested by Mendeleev, those of type i) turned out to be predominantly correct, while those of type ii) turned out to be predominantly false. As regards the placing of these elements, however, the picture is different: the placing of some of the elements subjected to type i) atomic-weight modifications encountered difficulties associated with the breakdown in the pattern of periodicity in the region of the periodic table between Ba and Ta (i.e. in the region occupied by the lanthamide elements); whereas the elements for which type ii) atomic-weight modifications were suggested were (apart from U) placed correctly by Mendeleev.[6]

In addition to using the periodic table for the modification of atomic weights, Mendeleev from the very outset of his work on the periodicity of the elements used the table also as a basis for the prediction of the existence and properties of unknown elements, and in a few cases also for the prediction of certain unknown chemical and physical properties of known elements.[7] Mendeleev's predictions of existence were based upon the occurrence of apparent gaps in the periodic table and the demand that these be filled; the prediction of physical and chemical properties was based upon the method of simple interpolation and (sometimes) extrapolation inherent in his concept of

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[5] Bibl.48, Section Seven: The Periodic Table Case Study.

[6] Concerning the criterion employed in this thesis for assessing the correctness of Mendeleev's placing of the elements, see Ch.III, n.249.

[7] Mendeleev predicted the existence of triethyl compounds for the known elements In and Tl (see Ch.V, p.318), and predicted certain additional properties for gallium (= "eka-aluminium") after he had learned of its discovery in 1875. He also predicted properties for known elements in certain cases where he had reservations about identifying the particular known element in question with the element whose properties he was predicting - as, for example, in the case of "dvi-boron"/yttrium (see section C of the present chapter).

"atomanalogy" (see Ch.V). Mendeleev's predictions of the existence and properties of unknown elements ranged from the unverbalised indications of merely existence which were implicit in his inclusion of dashes or question-marks in certain unoccupied places in the periodic table, to such predictions as those given for "eka-aluminium", "eka-boron" and "eka-silicon" which involved an explicit and most detailed consideration of physical and chemical properties.[8] The remarkable degree to which Mendeleev's predictions for eka-aluminium, eka-boron and eka-silicon were confirmed in the subsequent discovery of gallium, scandium and germanium, and the great significance which this had for the widespread recognition and acceptance of the periodic law, has tended to obscure both the fact that these predictions were not confirmed in every respect, and also the fact that Mendeleev predicted in addition the existence and certain properties of many other unknown elements (by no means always successfully).[9] The few instances where Mendeleev's predictions for eka-aluminium (= gallium), eka-boron (= scandium) and eka-silicon (= germanium) turned out not to be correct arose from his over-use of the method of simple interpolation from the properties of closest neighbours ("atomanalogues" or "atomologues") in the same series or same sub-group of the periodic table. Errors and inaccuracies in connection with his predictions of the existence and properties of other unknown elements arose sometimes out of a breakdown in validity of simple interpolation (drastically so for the region between Ba and Ta), and sometimes from an erroneous application of extrapolation at the edges of the table (Mendeleev himself was fully aware of the uncertainties of this method). Mendeleev's prediction of "eka-cadmium" and its properties represented the most detailed set of the erroneous predictions arising out of his extension of the pattern of periodicity shown by the lighter and heavier elements into that intermediate

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[8] Mendeleev denoted unknown elements, corresponding to gaps in his periodic table, by prefixing the Sanskrit words of counting to the names of the nearest lighter known elements in the same sub-group of the table: an adjacent higher unknown analogue of a known element X would thus be referred to as "eka-X", "eka" being the Sanskrit word for "one"; an adjacent higher unknown analogue of "eka-X" would be referred to as "dvi-X" ("dvi" = "two"), and so on for yet higher unknown analogues, using the prefixes "tri" ("three"), "chatur" ("four"), "pancha" ("five"), "shash" ("six"), etc. Although in explaining this system of nomenclature Mendeleev listed the Sanskrit numbers up to six in a manuscript passage (see Sc.Ar., 434), and up to four in his published work (see Annalen, 1871, p.196; PLBA, 150), he used only the first three prefixes - "eka", "dvi" and "tri" - in his actual discussions of particular unknown elements.

[9] Broadly speaking, the criterion used in this thesis for judgement of the correctness of Mendeleev's predictions is correspondence with present-day knowledge and beliefs concerning the existence and properties of elements and the structure of the periodic system.

region between Ba and Ta where, because of the lanthanide elements, it in fact breaks down. His most detailed series of false predictions made on the basis of extrapolation of the periodic table was that concerning the proposed lightest element x (or "newtonium", tentatively identified by Mendeleev with the luminiferous world-ether).

B. Mendeleev's use of the periodic system to determine the atomic-weight values of known elements

1. Type i) modifications: cases of drastic adjustment of the assumed atomic-weight value, involving a change in the accepted valency.

a) Beryllium

Although the magnesia-type formula had been proposed for beryllium oxide as early as 1842 by the Russian chemist Avdeev,[10] until the mid-1880's many chemists still favoured the alumina-type formula which had been proposed for this compound by Berzelius in the 1820's. The formula BeO demanded an atomic weight of ca. 9 for Be, whereas the formula Be_2O_3 demanded an atomic weight of ca. 14. Support for the alumina-type formula was at first based solely upon certain analogies between Al and Be, particularly the isomorphism of their oxides and the similar (amphoteric) chemical character of these oxides. But in 1878 this view received further apparent support from the specific-heat value (= 0.4079) determined for metallic Be by Nilson and Pettersson[11]: to satisfy the law of Dulong and Petit the atomic weight of Be could not be taken as 9, whereas the value 14 gave a reasonably satisfactory atomic-heat value of ca. 5.6. The late 1870's and early 1880's saw the height of the controversy over the formula of beryllia, the principal spokesman for the supporters of the formula BeO being the Czech chemist Brauner. Brauner opposed the formula Be_2O_3 on the grounds that a trivalent Be = 14 has no place in the periodic system, whereas divalent Be = 9 has a place in group II which corresponds to the majority of physical and chemical properties of the element.[12] By the mid-1880's support for the divalence of beryllium had been provided by Carnelley's determination of the melting-point of beryllium chloride[13], and by Burdakov's measurements of the density of aqueous solutions

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[10] See, for example, Ann.Chim., 7 (1843) 155. Mendeleev erroneously dated this contribution of Avdeev's to 1819 (see, for example, Pr.Ch., R-8, 1906, p.608; PLBA, 426).

[11] L.F. Nilson and O. Pettersson, Berichte, 11 (1878) 381-6.

[12] B. Brauner, Berichte, 11 (1878) 872; 14 (1881) 53.

[13] T. Carnelley, Phil. Mag. [5], 18 (1884) 1 - 22. The value of the melting-point determined experimentally by Carnelley for beryllium chloride (ca. 870°C) agreed well with the value he had predicted, on the basis of the trends which he had observed in the melting-points of the halides of the elements, for $BeCl_2$, and did not agree at all with his prediction for $BeCl_3$. However, Carnelley's experimental value for the melting-point of beryllium chloride has turned out to be quite wrong (as also have many of his other melting-point determinations); and in fact the correct value (ca. 405°C) agrees better with his prediction for $BeCl_3$ than with his prediction for $BeCl_2$.

of the chloride.[14] In 1884 Nilson and Petterson finally came to accept that beryllium is divalent, being persuaded by the results of vapour density measurements which they had carried out on the chloride. The evidence in favour of divalent beryllium became overwhelming when Humpidge in 1885 showed that at elevated temperatures the specific heat of metallic beryllium approaches a value which provides reasonable agreement with the law of Dulong and Petit for the atomic weight Be = 9.[15]

From the very beginning of his work on the periodic law Mendeleev had taken the atomic weight of Be to be ca. 9, classifying it as a divalent element occupying the place between Li and B in the periodic table. In his article of 1871 on The periodic lawfulness of the chemical elements (G.) he pointed out that not only does such a placing correspond well to the properties of beryllium, but also there is no possible place in the periodic table for a trivalent element of atomic weight ca. 14 with the properties of beryllium:

> Since the time of Avdeev's investigations different views have been held concerning the placing of beryllium in a system ... The periodic law gives the following in confirmation of the formula BeO. If the oxide of beryllium is given the formula of alumina, Be_2O_3, then the atomic weight of Be will be $\frac{3}{2}.9.4 = 14.1$, and it will then not find a place in the system, since it would have to be placed near nitrogen, where it would have to have distinctly acidic properties and give higher oxides of composition Be_2O_5 and BeO_3, which is not the case. But taking the oxide of beryllium to have the formula BeO, with Be = 9.4, it finds a place between Li = 7 and B = 11, which accords with the formula of its oxide and with all its properties. To demonstrate the latter, the following proportions will suffice:
>
> 1) Be:Li = B:Be ...
> 2) Be:Mg = Li:Na = B:Al ...
> 3) Be:Al = Li:Mg = B:Si ...
>
> Thus, all doubtful points regarding the position of Be in the system are elucidated. If Li, Na, K, Rb, Cs form one group, then Be, Mg, Ca, Sr, Ba form another, completely parallel in all respects.[16]

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[14] Burdakov's investigations (1884-5) were carried out at the suggestion of Mendeleev, and were based upon an empirical result by Mendeleev that for dilute solutions of the corresponding salts (e.g. the chlorides) of different metals, containing the same number of gram-molecules of salt dissolved in a given weight of water, a gradual increase in specific gravity is observed with increasing molecular weight of the dissolved salt at a given temperature. Burdakov's results suggested a molecular weight for beryllium chloride between that of KCl (74.5) and that of $MgCl_2$ (95), which is in accordance with the formula $BeCl_2$ (80) rather than $BeCl_3$ (120) (see Mendeleev's Faraday Lecture, 1889: PLBA, 228, footnote).

[15] Proc.Roy.Soc., 38 (1885) 188; 39 (1886) 1.

[16] Op.cit., pp. 165-7 (PLBA, 127-8).

The eventual triumph in the 1880's of Avdeev's suggestion of the magnesia-type formula for beryllia over Berzelius' suggestion of the alumina-type formula was seen by Mendeleev in his Faraday Lecture of 1889 as "having no less a significance for the history of the periodic law than the discovery of scandium, which in the hands of Nilson so clearly confirmed the prediction of eka-boron".[17]

b) Uranium

In his first published periodic table, table 8 (P1) (March 1869), Mendeleev classified uranium ("Ur") with an atomic weight of 116 between Cd = 112 and Sn = 118, as an analogue of B and Al. Mendeleev here appears to have taken the value 116 rather than the usual (Cannizzaro's) value of 120 for the atomic weight of uranium because there is no place in the periodic table for U = 120, whereas with an atomic weight between 112 (Cd) and 118 (Sn) uranium could be placed as a trivalent element in the same group as B and Al.[18] Mendeleev's first doubts about the atomic-weight value of 116 for uranium appear to have developed a little later in the spring of 1869, in connection with his study of the atomic volumes of the elements. By the early summer of the same year he had removed uranium from the place between Cd and Sn[19], on the grounds that U = 116 corresponds to an atomic volume which does not at all agree with the value expected for an element in this position in the periodic table. He now temporarily reverted to using Cannizzaro's atomic-weight value of U = 120[20], but only for want of a satisfactory alternative: because U = 120 finds no place in the periodic system Mendeleev felt that this value must certainly be wrong. With the revision of the atomic weight of uranium in mind he soon set one of his assistants, Bauer, the task of experimentally determining the specific heat of metallic uranium. This work was begun in the autumn of 1869 and was

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[17] PLBA, 228. The prediction of "eka-boron", and its confirmation in the discovery of scandium, is discussed in section C of the present chapter.

[18] See table 2 (M2) (a), a rough manuscript draft of table 8 (P1), where "120" Ur had been listed outside the table at the bottom of the page and then crossed out, and "Ur = 116?" included in the table itself; and see also conclusion 8 of Correlation of properties, quoted in Ch.III (p.168) of this thesis. The place between Cd and Sn into which Mendeleev put "Ur = 116" was in fact the rightful place of In, this latter element being placed unsatisfactorily as "?In = 75.6" in table 8 (P1) (see later).

Mendeleev's changing of the atomic weight of uranium from 120 to 116 is an example of what we have called a "type ii)" atomic-weight modification. It seems more natural to consider it here, in conjunction with the subsequent "type i)" modification suggested by Mendeleev for U, than later with Mendeleev's other "type ii)" modifications.

[19] Compare table 11 (M8) with table 12 (M9); and table 10 (P3) with table 13 (P4).

[20] See Sc.Ar., 82-3 (fotokopiia 9).

continued until the middle of 1870, but failed to give a positive result because of technical difficulties.[21] Nevertheless, even without the support of specific-heat data on the metal, early in 1870 Mendeleev came to suggest that the true atomic weight of uranium is double Cannizzaro's value, i.e. is 240 rather than 120, basing this proposal primarily upon the high value of the density of metallic uranium:

> Usually uranium U = 120 is included in the iron group,[22] because this ... metal forms a suboxide U_2O, UO and an oxide U_2O_3, just as do the elements of the iron group ...[23] But along with this similarity to the elements of the iron group, uranium has also many distinctive properties which compel us to be cautious in assuming its resemblance to iron ... If we retain those formulae for uranium compounds which Peligot gave them [sc. those formulae corresponding to the atomic weight U = 120], then uranium presents - according both to its physical properties and to the acidic character of its oxides - a rather more significant resemblance to such heavy metals as the platinum metals, and perhaps there is an error in the determination of its atomic weight. Perhaps the atomic weight of uranium should be doubled, because, among other things, such heavy (density 18.4) metals as uranium are encountered only among the elements of high atomic weight, examples being Pt, Os and Ir, with atomic weights of ca. 197, density ca. 22. Resembling these are palladium, rhodium and ruthenium, with density ca. 11 and atomic weight ca. 105 ... Uranium seems to stand in the same sort of relationship to the elements of the iron series as do platinum and palladium; its atomic weight (120) and its density are about twice those of iron and its analogues. But whereas the atomic weight of uranium at present approximates to those of palladium, rhodium and ruthenium, its density is nearly twice theirs. Lead (density 11.3), mercury (13.6), gold (19.3) and certain other elements having considerable densities have at the same time also large atomic weights, viz. ca. 200. If the atomic weight of uranium is doubled to U = 240, then the oxide of uranium, UO_3, presents an analogy with SO_3, CrO_3, the suboxide UO_2 is an analogue of SO_2, TeO_2, SnO_2, and the following become clear: 1) the absence of UCl_6, just as there is no $CrCl_6$, $TeCl_6$, etc.[24]; 2) the volatility of UCl_4, resembling the volatility of $SnCl_4$, etc.; 3) the tendency to give the lowest degree of combination with chlorine, because $TeCl_4$ also loses part of its chlorine[25]; 4) the incapacity of uranium oxide to give alums,

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[21] The difficulty was that of fusing powdered uranium metal to obtain cast-uranium; Mendeleev was not convinced of the purity of the powdered samples of the metal which he and Bauer had obtained (see, for example, Annalen, p.183; PLBA, 140).

[22] Mendeleev does not mean here that U = 120 was included in the iron group in the periodic table, which indeed it was not, but merely that it tended to be considered an analogue of iron.

[23] The portion of the passage which has here been omitted consists of a short list of other similarities between uranium (taken as U = 120) and the elements of the iron group.

[24] The point which is being made here seems to be merely that since other elements which form oxides RO_3 do not form chlorides RCl_6, there is no reason to expect that uranium should form such a chloride. (Actually, uranium does give the compound UCl_6, but this was not recognised until after Mendeleev's death).

[25] This is a reference to the formation of UCl_3 (taking U = 240), seen as analogous to the formation of $TeCl_2$, as is made clear by a related more explicit remark by Mendeleev in his Annalen paper of 1871, p.182 (PLBA, 139).

such as analogous oxides form[26]; 5) the weak acidic properties of uranium oxide, UO_3, like CrO_3, TeO_3; 6) the basic properties of this same oxide ... But in order to confirm or refute such a suggestion about the atomic weight of uranium it would be necessary: 1) to determine the vapour density of the volatile uranium chloride, which may be UCl_2 (U = 120) or UCl_4 (U = 240); 2) to study the lowest degree of combination of uranium; 3) to determine the specific heat of the metal itself and its compounds; 4) to study the crystalline forms of the compounds of uranium suboxide, and so on. While this remains unknown we cannot confirm the analogy of uranium oxide to Fe_2O_3, Cr_2O_3, Al_2O_3, etc., or to SO_3, CrO_3, FeO_3, etc. The absence in uranium of the tendency to further oxidation, and the known specific heat of the suboxide of uranium, tend to support the latter suggestion.[27]

The earliest known periodic table in which Mendeleev included U = 240 (as a higher analogue of Cr, Mo and W) seems to have been the short-form manuscript table 17 (M11), dating from the summer-early autumn of 1870. It was at about this time that he began to include in his short-form periodic table also the seven elements In, Th, Yt, Ce, La, Di and Er, altering their atomic weights from the generally-accepted values in doing so (see below). The placing of U and these latter 7 elements in the table was, as may be expected, a task which involved Mendeleev in much consideration of the mutual relationships among these elements; in a number of cases the placing of one element indicated the way for the placing of another.

The classification proposed by Mendeleev in 1870 of uranium as a higher analogue of Cr, Mo and W with an atomic weight of 240 was retained by him throughout his life.[28]

The first published periodic table in which Mendeleev classified uranium as U = 240 was table 30 (P7), given in his article A natural system of the elements (R; publ. Feb. 1871). In the text of this article, and in the articles On the place of cerium (G.; publ. March 1871) and The periodic lawfulness of the chemical elements (G.; publ. Nov. 1871), Mendeleev discussed at some length the question of the placing of U (and of In, Th, Yt, Ce, La, Di and Er) in the periodic table, and, as in the March 1870 instalment of his Principles of Chemistry (see above), suggested various experimental means by

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[26] By "analogous oxides" Mendeleev seems to be referring here to such oxides as Fe_2O_3, Cr_2O_3, Al_2O_3, viz. those oxides seen as analogous to uranium oxide if U = 120.

[27] Pr.Ch., R-1, 3rd instalment (March 1870), pp.381-3 (part II, 1871); PLSM, 295-8.

[28] In the 1890's and early 20th century Mendeleev took the atomic weight of U to be not exactly 240 (H=1) as he had earlier, but slightly less, the lowest value being U = 238.5 (O=16) given in tables 62, 63 and 64.

which the atomic-weight value U = 240 could be tested.[29] Strong empirical support for this value U = 240, resulting in its general adoption, was provided during the subsequent decade, particularly by Roscoe's comparative studies of U with Cr, Mo and W (1874)[30] and by Zimmerman's determination of the vapour densities of uranium chloride and bromide (1880-2).[31]

In the later editions of Principles of Chemistry Mendeleev referred to the significance which he saw for the periodic law in the confirmation of the atomic-weight value U = 240: in the 8th (1906) edition, for example, he wrote -

> ... uranium ... has played a prominent role in the confirmation of the periodic law, because with the recognition of this law a change in its atomic weight (from U = 120 to U = 240) was called for, and was proved valid (by Roscoe, Rammelsberg, Zimmerman and others), and for me this has served (together with the atomic weights of Ce and Be) as convincing evidence of the generality of the periodic law.[32]

c) Indium, thorium and cerium[33]

From the time of his discovery of the periodic law (Feb., O.S., 1869) up to the summer-early autumn of 1870 Mendeleev assumed the following atomic weights for In, Th and Ce -

In : ca. 75,
Th : 115 - 118,
Ce : 92,

taking all three elements to be divalent in their usual oxides.[34] These three elements were included in his manuscript "attempt at a system" table 3 (M3) and its published counterparts tables 8 (P1) and 9 (P2), but only in a most unsatisfactory manner in two "tails" at the bottom of the table. Mendeleev had originally attempted, in table 2 (M2), to place In ("75.6?", "72?") in the main (central) part of the table, trying two different places next to Zn, but had then crossed out these entries. Apart from table 11 (M8) (spring 1869), which contains In (75.6) and Ce (92), no other periodic table drawn up by Mendeleev included In, Th or Ce until the summer-early autumn of 1870, when

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[29] See especially The periodic lawfulness of the chemical elements (G.; 1871), pp.178-84 (PLBA, 136-41).

[30] H.E. Roscoe, J.Chem.Soc., 27 (1874) 933; Berichte, 7 (1874) 1131.

[31] J.L.C. Zimmerman, Annalen (Liebig), 204 (1880) 204; 216 (1882) 1.

[32] Pr.Ch., R-8 (1906) 733 (PLBA, 523). Rammelsberg's studies of the properties of uranium, referred to here, were published in Berichte, 5 (1872) 1003.

[33] Further aspects of Mendeleev's views on cerium are considered in section B of Ch.VII.

[34] The correct formulae for these usual oxides are In_2O_3, ThO_2 and Ce_2O_3, i.e. with In and Ce trivalent and thorium tetravalent.

the atomic-weight values of these elements were changed by him as follows -

In : to 113,

Th : first to 174, then very soon to ca. 230,

Ce : to 138[35].

The atomic-weight values which Mendeleev had taken for In and Ce in Feb.-March 1869, viz. ca. 75 and 92 respectively, were those assumed by the overwhelming majority of chemists at the time. The atomic weight Th = 115 - 118 on the other hand, although still commonly accepted, had already been rejected by many chemists (probably not a majority, but at least a sizeable minority) in favour of the value of ca. 230, corresponding to tetravalent Th, on the basis of the analogies demonstrated between Th and Zr by Delafontaine and by Chydenius in 1863. (Newlands and Odling, for example, had adopted a value of ca. 230 for the atomic weight of thorium as early as 1864). Mendeleev himself had in 1868 noted that "the rare mineral thorite [sc. a thorium silicate] resembles zircon [sc. a zirconium silicate]";[36] furthermore, although in his "attempt at a system", 1869, he had entered thorium as "Th = 118?", he had written at the top of the sheet on which he drew up the rough-draft manuscript form of this "attempt", table 2 (M2), the names of Chydenius and Delafontaine, the oxide-formula ThO_2, and the corresponding atomic-weight value for Th of 230.

In his first article on the periodic law, Correlation of properties (written March 1869), Mendeleev acknowledged the uncertainty of the atomic-weight values he had assumed for In and Th (and also for certain other elements, of which he mentioned only yttrium by name).[37] He did not again touch upon the subject of the atomic weight of thorium, its position in the periodic table, or its chemical analogies with other elements, until after his adoption of the atomic-weight value of ca. 230 for this element in the summer-early autumn of 1870. For indium, however, and also for cerium, such matters were considered by him later in 1869 and in the first half of 1870. In his remarks on cerium during this period Mendeleev tended to associate this element, together with La and Di, with the elements of the iron, palladium and platinum families (for details, see section B of Ch. VII); as regards the

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[35] These new values correspond in the cases of In, Ce and Th = ca. 230 to the correct formulae of the usual oxides of these elements, and in the case of Th = 174 to the incorrect formula Th_2O_3.

[36] Pr.Ch., R-1, 1st instalment (1868), p.73 (part I, 1869); PLSM, 282.

[37] Op.cit., p.73 (the passage in question has already been quoted in Ch.III, p.167).

atomic weight of cerium, he gave no indication of doubting the value Ce = 92 before the summer-early autumn of 1870. His comments before mid-1870 on the placing of indium in the periodic table contain two proposals, related to the erased entries "In = 75.6?" and "In = 72?" in the central region of table 2 (M2), viz. placing indium in the group Be, Mg, Zn, Cd between Zn and Cd, or, alternatively, placing it in the B - Al group in the place corresponding to the as yet undiscovered gallium. In his Correlation of properties Mendeleev wrote, "In this column [sc. the column containing Nb in a horizontal short-form table such as table 10 (P3)], in the group of magnesium, zinc and cadmium, it seems that we should place indium (In = 75.6?), if indeed it belongs to this row (it is less volatile than Zn and Cd)".[38] Shortly afterwards he included In = 75.6 between Zn and Cd in the manuscript table 11 (M8). But whereas the place suggested for In between Zn and Cd in Correlation of properties appears to be that which actually corresponds to Sr, in table 11 (M8) both In and Sr are included between Zn and Cd, with Sr in its proper place and In merely inserted between rows, between Zn and Sr. Later in 1869, in his paper on Atomic volumes, Mendeleev made the following suggestion:

> ... we may say that those two elements which are still missing from the system and which should show a resemblance to Al and Si, and have atomic weights of about 70,[39] will ... occupy in all respects a mean, or constitute a transition, between zinc and arsenic. Perhaps In occupies just this place in the Al row, if there is a mistake in its determined atomic weight arising perhaps from incomplete purification from heavier metals (perhaps Cd).[40]

In the 3rd instalment (March 1870) of the 1st edition of Principles of Chemistry Mendeleev discussed In in conjunction with Zn and Cd; but in addition to recognising similarities to Zn and Cd shown by In he pointed out also certain differences, e.g. the lower volatility of In than of Zn and Cd, and the fact that indium oxide does not dissolve in ammonia whereas the oxides of Zn and Cd do.[41]

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[38] Op.cit., p.72 (PLBA, 26).

[39] These are the elements Ga and Ge, unknown at the time, and referred to by Mendeleev from late 1870 until the time of their discovery as "eka-aluminium" and "eka-silicon" respectively.

[40] Op.cit., p.67 (PLBA, 42).

[41] Pr.Ch., R-1, part II: Colls., 14, 187.

Mendeleev's incorporation of In, Th and Ce into the periodic table with modified atomic-weight values in the summer-early autumn of 1870 is first seen in table 16 (M10), which has all three of these elements listed in the B - Al group (which was soon to be labelled "group III") as "In = 113.4", "Ce = 138" and "?!Th = 174".[42] Very shortly afterwards, in table 17 (M11), Mendeleev came to adopt the atomic-weight value Th = 231, now placing this element as an analogue of Ti and Zr (i.e. in what was soon to be called "group IV"); in the same table he included Ce = 138 in both "group III" and "group IV". In table 19 (M13), still in the summer-early autumn of 1870, Ce was placed in "group IV" only; the placings of In, Th and Ce given in this table were retained by Mendeleev throughout his life.[43]

"In = 113.4" was placed in table 16 (M10) in the space which had become vacant as a result of Mendeleev's removal of "Ur = 116" from the periodic table; in drawing up table 16 (M10) Mendeleev had originally put "Th? = 118?" in this space, but had then crossed out this entry and replaced it with "In = 113.4". Such a placing of indium next to cadmium, but in a different group, corresponded to the degree of analogy shown between these elements while at the same time explaining their differences: this has already been pointed out by Kedrov, who has also suggested, not implausibly, that Mendeleev's placing of indium in group III may have been influenced by the fact that in the previous year he had come to place thallium in this group, thallium being an element which had been discovered not only at the same time as indium but also by the same (spectral) means.[44] What Kedrov does not mention, however, is the distinct possibility that Mendeleev was influenced in his placing of indium in group III as In = 113.4 by Lothar Meyer's suggestion of the very same placing and atomic weight for this element some months earlier (see Fig. III-14, given on p.155). Mendeleev himself never acknowledged any such influence, but the fact remains that although he had expressed doubts about the atomic-weight value In = ca. 75 as early as March 1869 there is no evidence of his suggesting the value 113.4 until the

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[42] Also in table 16 (M10), in "group III", is the entry "Ce La Di 92"; "Ce 138" had been subsequently added to the table, but the original entry for Ce had not been crossed out.

[43] Of these final placings by Mendeleev of In, Th and Ce in the periodic table, only that of In is consistently adhered to in modern periodic tables; Th is sometimes placed today as it was by Mendeleev, but Ce never so.

[44] Kedrov, Sc.Ar., 803.

summer-early autumn of 1870; and in the meantime he had seen Meyer's publication of March 1870 in which indium is placed in the B - Al group as In = 113.4 (Mendeleev had referred to Meyer's 1870 article within weeks of its publication - see earlier, Ch.III, p.155).

Mendeleev's placing of thorium as Th = 231 in table 17 (M11) was almost certainly encouraged by the fact that an extra row at the end of the table, into which Th = 231 could be fitted, was necessitated by the inclusion of U = 240. His eventual placing of Ce = 138 in "group IV" rather than "group III", corresponding to the highest oxide CeO_2, was probably to some extent encouraged by this placing of Th = 231 in "group IV".[45]

In the early autumn of 1870 Mendeleev wrote in outline a short manuscript note on indium in which he pointed to certain analogies of this element to aluminium (e.g. precipitation by $BaCO_3$) in support of the atomic weight In = 113.4,[46] and where he expressed the need for investigating the specific heat of metallic indium and the tendency of the element to alum-formation, noting that if the atomic weight is In = 75.6 the specific heat should be 0.083 whereas for In = 113 the specific head should be 0.055. Soon afterwards he set out to measure the specific heat of metallic indium himself, using a small mercury calorimeter of his own construction. Preliminary results gave a value of 0.055, supporting the atomic weight In = 113.4. The value of 0.057 obtained by Bunsen, published in September 1870, confirmed Mendeleev's as yet unpublished result.[47]

In two manuscript drafts of the proposed article Towards a system of the elements, written in the autumn of 1870, Mendeleev again presented the points he had outlined in his slightly earlier manuscript note on the atomic weight of indium, and also referred to Bunsen's experimental determination of the specific heat of metallic indium.[48] He discussed in addition the question

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[45] Kedrov (Sc.Ar., 808) suggests, conversely, that Mendeleev's placing of Th in "group IV" was encouraged by his placing of Ce in this group. However, since in table 17 (M11) the placing of Th in "group IV" seems to have been more definite than the placing of Ce in this group (as "?Ce = 138", as opposed to "Ce = 138" in "group III"), I cannot agree with Kedrov's suggestion.

[46] The empirical data to which Mendeleev refers in this manuscript note had been obtained by R.E. Meyer, C. Winkler and others, two or more years earlier (see Sc.Ar., 106).

[47] Bunsen, Annalen (Pogg), No. 9, Sept. 1870. In his article On the history of the periodic law (G.), Berichte, 13 (1880) 1796-1804, Mendeleev wrote (op.cit., p.1800; PLBA, 401): "I made my determination of the specific heat of indium before I learned of Bunsen's determination, but the results were published after ... because I wanted to make determinations also of the specific heats of cerium and uranium".

[48] See Sc.Ar., 128-31, and 132-7.

of the atomic weight and placing in the periodic table of cerium: he cited as support for the placing of cerium as Ce = 138 in group IV the specific-gravity sequence Ti-Zr-Ce, and the fact that for Ce = 138 the highest oxide of this element is CeO_2, which is the very form demanded for an element of group IV; in the second of the two manuscripts he suggested three experimental paths by which his proposed atomic-weight value and placing of cerium could be tested - i) the determination of the specific heat of cerium metal, ii) the comparative study of the compounds Ce_2O_3, In_2O_3 and Al_2O_3, and iii) the comparative study of the compounds CeO_2, TiO_2, SnO_2 and ZrO_2.[49] Also in the second of these manuscripts he expressed the view that "The judgments based upon the study of the compounds of cerium will perhaps extend to the other cerites [sc. La, Di] and to the gadolinites [sc. Y, Er]".[50]

Early in November 1870 Mendeleev himself experimentally determined the specific heat of cerium as ca. 0.05, which agreed with the change he had proposed for the atomic-weight value of this element.[51]

The atomic weights and placing in the periodic table of In, Th and Ce (and also of U, La, Di, Y and Er) were discussed in some detail in Mendeleev's articles On the place of cerium (G.; written Nov. 1870, publ. March 1871) and A natural system of the elements (R.; written Nov.-Dec. 1870, publ. Feb. 1871). In On the place of cerium the atomic weights In = 113, Ce = 138 and Th = 231 are given; in A natural system of the elements we find In = 113, Ce = 138? and Th = 232. In February 1871, in table 31 (P8), Mendeleev adopted the atomic-weight value Ce = 140,[52] primarily for the sake of better regularity of atomic-weight differences in the periodic table rather than for empirical reasons; later in the same year, in his article The periodic lawfulness of the chemical elements (G.), he wrote -

> ... because Ba = 137 we should expect that the atomic weight of cerium will in the future be determined to be higher than it is at present, since at the moment it is very close to the atomic weight of barium ... Slight admixture with Di and La, and also the difficulty of analysis which has been pointed out by Marignac, and the difficulty in obtaining the suboxide of cerium free from cerium oxide, may justify the slight increase in the atomic weight of cerium which can

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[49] Sc.Ar., 137.

[50] Ibid.

[51] See On the place of cerium (G.), publ. March 1871 (PLBA, 59-67).

[52] This is an example of what we have called a "type ii)" atomic-weight modification.

> be expected on the basis of the periodic law; and therefore in the tables adopted by me [sc. tables 35 (P11) and 36 (P12)] I have taken the atomic weight of Ce provisionally as 140.[53]

The atomic-weight value of ca. 140 rather than ca. 138 for Ce was subsequently confirmed empirically, e.g. in Brauner's experiments of the early 1880's.

Although from late 1870 onwards Mendeleev consistently placed cerium in the periodic table as a higher analogue of Zr in group IV, with an atomic-weight value in the region of 140, he nevertheless expressed a slight lingering doubt about this atomic weight and placing in his 1871 article on The periodic lawfulness of the chemical elements, as indeed is reflected in table 36 (P12) which accompanied this article, where the entry for cerium is preceded by a question-mark, "?Ce = 140". This doubt arose for Mendeleev from the uncertainty which still remained concerning the atomic weights and placing in the periodic table of such elements as La, Di and Y which have equivalent weights close to those of Ce in its oxide and suboxide, and also from the observation that CeO_2 (assuming Ce = ca.140) is much more readily reducible than is ThO_2, contrary to the usual tendency for the highest members of a group to be the most readily reducible.[54] Two years later (1873), in an article criticising Rammelsberg's support for the atomic weight Ce = 92,[55] Mendeleev explicitly withdrew this expression of doubt which he had made in 1871 concerning the placing of Ce in the periodic table.[56] In this article of 1873 Mendeleev convincingly showed that the analyses of cerium compounds which Rammelsberg had presented as evidence in support of Ce = 92 in fact fitted more closely the formulae based upon an atomic weight for cerium in the region of 140.

In his Note in connection with the discovery of gallium (F.), 1875, Mendeleev listed the changes he had proposed on the basis of the periodic law for the atomic weights of In, Th and Ce, and referred to the empirical evidence in support of these changes.[57] (At the same time he listed also the atomic-weight changes which he had proposed for uranium, yttrium, erbium, lanthanum and didymium).

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[53] Op.cit., p.187, footnote (PLBA, 143).

[54] See The periodic lawfulness of the chemical elements (G.), 1871, p.189 (PLBA, 144-5).

[55] Rammelsberg, Berichte, 6 (1873) 84.

[56] On the applicability of the periodic law to the cerite metals (R.) J.Russ.Chem.Soc. and Phys.Soc., 5 (1873) no. 3, section 1, pp.119-130; p.120, footnote (PLBA, 185-6).

[57] Comptes Rendus, 81 (1875) 970 (PLBA, 200).

d) Yttrium, erbium, lanthanum and didymium

The changes proposed by Mendeleev in the atomic-weight values of yttrium, erbium, lanthanum and didymium, and his associated suggestions concerning the placing of these elements in the periodic table, were subsequent to, and influenced by, the atomic-weight modification and eventual placing in the table which he suggested for the better-characterised cerium in the summer-early autumn of 1870. The atomic-weight values adopted by him for yttrium, erbium, lanthanum and didymium in late 1870/early 1871, compared with those values which he had assumed for these elements in March 1869, are indicated below:

Element	At.wt. assumed by Mendeleev in March 1869	At.wt. adopted by Mendeleev in late 1870/early 1871
Yttrium	60	ca. 90
Erbium	56(→112.6 by 1870)	135 - 180
Lanthanum	94	
Didymium	95	

The details of the atomic-weight changes proposed by Mendeleev for these elements, and of his placing of them in the periodic table, are considered in Ch.VII.

2. Type ii) modifications: cases of relatively slight adjustment of the assumed atomic-weight value, with the assumed valency remaining unchanged[58]

a) Titanium

The atomic weight of titanium had been determined as 48.27 by Rose in 1829.[59] In 1847 Pierre obtained the value Ti = 50.0[60]; this was the most commonly assumed value for titanium at the time of Mendeleev's discovery of the periodic law, and was the value assumed for this element in Mendeleev's earliest periodic tables. In late 1870-early 1871, however, Mendeleev came to adopt the value Ti = 48, retaining this value in all of his subsequent work.[61]

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[58] Some type ii) atomic-weight modifications have already been mentioned in the course of the above discussion of type i) modifications, e.g. that of U = 120 to U = 116 during Mendeleev's construction of his original "attempt at a system".

[59] Ann.Phys., 15 (1829) 145.

[60] Ann.Chim.Phys. [3], 20 (1847) 257.

[61] The value Ti = 48 had been adopted by Lothar Meyer as early as 1864 (see Fig.III-12), and by Odling in 1865 (see Figs. III-7 and III-8; in Odling's 1864 table on the other hand, Fig. III-6, we find "Ti 50").

The first signs of Mendeleev's doubt about the value Ti = 50 date from November (O.S.) 1870: tables 24 (M17), 25 (M18) and 26 (M19) have the entry "Ti = 50?",[62] and in his article A natural system of the elements (R.) Mendeleev says, "The transition from Ca = 40 to Ti = 50 is very rapid, but from Ti = 50 to V = 51 very slight, and if titanium were actually to possess an atomic weight of about 48 then the relationship of its atomic weight to the weights of its neighbouring elements would be more regular";[63] in this same article he suggests that those experimental determinations of the atomic weight of titanium which had given a value of ca.50 rather than ca.48 had perhaps used titanium containing small amounts of a heavier impurity such as "eka-silicon" (germanium).[64] In his article on The periodic lawfulness of the chemical elements (G.), 1871, Mendeleev cited the atomic-weight determinations of Rose as support for adopting the value Ti = 48, and again suggested that the higher values which had been found had perhaps arisen from contamination of the titanium with the heavier "eka-silicon".[65] Tables 35 (P11) and 36 (P12) which accompany this article contain the entries "Ti = 48?" and "Ti = 48" respectively.

Extensive researches by Thorpe in the early 1880's confirmed the atomic weight Ti = 48[66], as was pointed out by Mendeleev in his Faraday Lecture of 1889.[67] However, Mendeleev's suggestion that higher values had arisen from "eka-silicon" (germanium) contamination of titanium was not vindicated; germanium (discovered 1886) did not turn out to be a natural contaminant of titanium.

b) Tellurium and iodine

The pair of elements Te and I is one of 4 pairs of elements in the modern periodic table where a decrease of atomic weight occurs with an increase in atomic number, the modern atomic-weight values of these elements being Te = 127.6 and I = 126.9.[68] At the time of Mendeleev's discovery of the periodic law the atomic weights of tellurium and iodine were usually taken as Te = 128 and I = 127, i.e. at that time also the generally-accepted

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[62] The corresponding published tables 33 (P10) and 30 (P7) similarly contain 'Ti = 50?'.

[63] Op.cit., p.52 (PLBA, 98).

[64] Ibid. (PLBA, 97-8).

[65] Op.cit., p.203 (PLBA, 155).

[66] Berichte, 16 (1883) 3014; Chem. News, 48 (1883) 251; Proc.Roy.Soc., 36 (1884) 43; Chem. News, 51 (1885) 260; J.Chem.Soc., 47 (1885) 108.

[67] PLBA, 229.

[68] The other 3 such pairs are Co - Ni (see below), Ar - K (see below) and Th - Pa (this pair did not concern Mendeleev).

atomic-weight values of Te and I were such that if these elements were to be given the places in the periodic table which were demanded by their chemical analogies, then they would present a deviation from the order of increasing atomic weight. Since the principle of atomic-weight ordering was fundamental to Mendeleev's periodic system (as distinct from the modern periodic system, where the ordering of the elements is according to "atomic number", or nuclear charge), the values Te = 128 and I = 127 could not both be accepted by Mendeleev without the very foundation of his system being undermined. Consequently, from the time of his discovery of the periodic law right up to the end of his life Mendeleev questioned the reliability of the experimental data which had led to the atomic weight of Te being taken as greater than that of I. Before the mid-1890's Mendeleev's doubts in this connection seem to have been directed only towards the atomic weight Te = 128, the value I = 127 apparently being accepted by him at this time. After 1895, however, he came to express doubts also about the value I = 127. This broadening of Mendeleev's field of doubt in connection with the atomic-weight values of the pair of elements Te and I is to be attributed to the experimental results obtained in 1895 by Brauner, these results indicating an atomic weight for tellurium greater than 127, and not equal to 125 as had been indicated by earlier results obtained by the Czech chemist.

In his Correlation of properties (R.; written March 1869) Mendeleev had concluded, on the basis of his classification of the elements in table 9 (P2), that, "The value of the atomic weight of an element may sometimes be corrected in the light of our knowledge of its analogies. Thus, must not the atomic weight of Te be 123-126, and not 128?".[69] Nevertheless, up to February 1871 the value Te = 128 was retained (although usually followed by a question-mark) in all of the periodic tables published by him which included the atomic-weight values of the elements.[70] In table 31 (P8), published in late February 1871, Mendeleev included tellurium as "Te = 125 (?128?)"; apart from table 33 (P10), which lists tellurium as "Te = 128?",[71] Mendeleev's subsequent periodic tables published before the late 1890's consistently gave the atomic-weight value of Te as 125.[72]

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[69] Op.cit., pp.76-7 (PLBA, 31).

[70] Mendeleev did, however, include tellurium with an atomic weight of 125 in a number of his manuscript tables during the period March 1869-late 1870, the earliest known instance of this being in table 5 (M5) (March 1869).

[71] Although table 33 (P10) was not published until March 1871, it had been drawn up as table 25) in early December 1870.

[72] Tellurium was entered in these tables sometimes as "Te=125", sometimes as "Te=125?", and in one case (table 38) as "Te=125(128?)".

The question of the atomic weight of tellurium was discussed by Mendeleev in his 1871 article on The periodic lawfulness of the chemical elements (G.) as follows:

> ... tellurium, judging from the periodic law, must have an atomic weight greater than Sb = 122 and less than I = 127, i.e. tellurium must be approximately Te = 125, because it occupies in all respects a mean atomological position between Sb and I. Judging from the fact that Ag-Cu = 45, Cd-Zn = 47, Sb-As = 47, I-Br = 47, Cs-Rb = 48, Ba-Sr = 50, we must think that Te-Se will also be close to 47, since Te stands between Sb and I just as Se stands between As and Br. And since the atomic weight of Se = 78, and it has been better studied and is more easily purified than Te so that its determination may be trusted more than the determination of the atomic weight of tellurium, the latter should therefore be close to 78+47 = 125 ... [But in accordance with the experimental results obtained by Berzelius and by Hauer] the atomic weight Te = 128 is usually assumed ... It is impossible to think that the individual differences of tellurium should have determined for it so considerable a deviation (128-125) from the value of the atomic weight which it ought to have according to the law of periodicity; a new experimental determination of its atomic weight is needed, giving an idea of the degree of applicability of the law of periodicity to the correction of atomic-weight values.[73]

To an off-print of this 1871 article on The periodic lawfulness of the chemical elements Mendeleev appended a manuscript note indicating that he felt that perhaps the "tellurium" which had given an atomic-weight value of ca. 128 was in fact a mixture of 93% tellurium (Te = 125) and 7% "eka-tellurium" (= 173);[74] in "Tabelle II" (i.e. table 36) of this off-print the atomic-weight value "173" was pencilled into the place corresponding to "eka-tellurium".[75]

Prompted by Mendeleev's comments in The periodic lawfulness of the chemical elements (1871) on the question of the atomic weight of tellurium, Brauner in the early 1880's began an experimental determination of the atomic weight of this element.[76] In August 1883, at the Odessa Congress of Russian Scientists and Physicians, he reported that he had found Te = 125. Mendeleev was not present at this congress, but the participants sent him a

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[73] Op.cit., pp.209-10 (PLBA, 160-1). This passage immediately follows the passage already quoted in Ch.V, pp.296 - 7, on the "individual deviations" in the atomic weights of the elements.

[74] This manuscript note runs as follows: "7% of the 1st analogue of Te or Ekatell= 173" (see PLSM, 468).

[75] See Sc.Ar., 369.

[76] An account of Brauner's contribution to the investigation of the atomic weight of tellurium is given by Kedrov in Bibl.38, pp.91-7.

congratulatory telegram informing him of Brauner's confirmation of his prediction that the atomic weight of tellurium should be ca. 125[77]. In September 1883 Brauner again reported on his work on tellurium, at a meeting of the Chemical Section of the Russian Physico-Chemical Society in St. Petersburg at which Mendeleev was chairman.[78] Three years later (1886), on the grounds of Brauner's determination of Te = 125, Mendeleev listed the Czech chemist among four chemists whom he saw as "consolidators of the periodic law".[79]

In 1889 Brauner obtained new results in connection with the determination of the atomic weight of tellurium, which again indicated a value Te = 125. In the same year Mendeleev wrote, in his Faraday Lecture, "Professor B. Brauner ... has shown by a series of analyses that the true atomic weight of tellurium is in fact less than that of iodine, and is close to 125".[80] In 1895, however, Brauner obtained further experimental results which indicated an atomic weight for tellurium greater than that of iodine, i.e. greater than 127.[81] Brauner felt that these results had arisen from the presence of some heavier impurity in admixture with the tellurium; Mendeleev, on the other hand, although not rejecting this possibility,[82] at the same time now came to think that perhaps it was an error in the determined atomic-weight value of iodine which led to the anomalous ordering of the atomic weights of Te and I. In 1898 Mendeleev wrote:

> As regards the atomic weights of Te and I, according to the periodic law we should think that the atomic weight of iodine is greater than that of tellurium. But because the determinations of Brauner, who has always defended and supported the periodic law, give Te = 127.5, and the determinations of Stas give I = 126.85, i.e. the opposite order to that demanded by the periodic law, then before changing our minds again over the difficult question of the purity of Te or seeking in it heavier impurities (as Brauner thinks), it seems to me that we should re-determine, after every possible purification of iodine, the value of its equivalent, because in spite of the precautions taken by so

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[77] See Kedrov, Bibl. 38, p.92.

[78] J.Russ.Phys-Chem.Soc., 15 (1883), section 1, p.433.

[79] This was a manuscript comment (see PLSM, 676-7). The other 3 "consolidators (ukrepiteli) of the periodic law" whom Mendeleev listed in this manuscript were de Boisbaudran, Nilson and Winkler, the discoverers of Ga, Sc and Ge respectively.

[80] PLBA, 229.

[81] See Kedrov, Bibl. 38, pp. 94-5.

[82] In a footnote newly appended to his Faraday Lecture in the 2nd edition (1895) of his Two London lectures (R.) Mendeleev suggested that if Brauner's idea of a heavier impurity in tellurium be correct, then perhaps this impurity is "dvi-tellurium", with an atomic weight of ca.212 (see PLBA, 229). (Contrast Mendeleev's manuscript suggestion of 1871, noted earlier, that tellurium perhaps contains "eka-tellurium", of atomic weight 173, as impurity).

> powerful a researcher as Stas it is still possible to think that in his iodine there may have remained some chlorine or bromine impurity which would decrease the atomic weight of the iodine.[83]

Elsewhere in the same article, in a footnote, Mendeleev commented, "Most probably, as also is maintained by Brauner, there is in tellurium an as yet undetermined admixture of an element with greater atomic weight; but it is impossible also not to express the wish that the atomic weight of iodine be newly checked, that perhaps this will lead to the necessity to increase its atomic weight".[84] In his subsequent comments on the question of the atomic weights of the pair of elements Te and I, Mendeleev continued to recognise the possibility of an error in the commonly-accepted values for both elements, not just in the value for a particular one of them as he had done prior to 1895.[85] In his periodic tables published at this time he gave the atomic weights of these elements as Te = 127, I = 127, e.g. in tables 57 (P30) and 63 (P36).

c) Osmium, iridium, platinum and gold

By the end of 1870, on the basis of a consideration of the chemical analogies of Os, Ir, Pt and Au with other elements, Mendeleev had placed these four elements in their correct order in the periodic table (see Fig. III-20, p.194). His first periodic tables to include these elements in their correct order gave the currently-accepted empirical atomic-weight values Os = 199, Ir = 198 or 197, Pt = 197, Au = 197, but since these values did not correspond to the order of the elements in the table Mendeleev appended question-marks to the values for Os, Ir and Pt (see the manuscript tables 23, 24, 25, 26 and the corresponding published tables 30 and 33). In table 31 (P8), drawn up and published in February 1871, Mendeleev adopted the values Os = 193, Ir = 195, Pt = 197, Au = 197, not on empirical grounds but solely to bring the atomic weights of the platinum elements into line with the demands of atomic-weight ordering. Later in 1871, in the tables 35 (P11) and 36 (P12) included in The periodic lawfulness of the chemical elements (G.), he went further and removed the equality of values in the case of Pt and Au, giving the series Os = 195, Ir = 197, Pt = 198, Au = 199. In the text of this article he wrote, "According to Berzelius and Fremy, Os = 199-200, Ir = 197, Pt = 198, whereas the following series would be expected: taking

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[83] Bibl.11, vol.23, half-vol. 45, 1898, p.322 (PLBA, 269).

[84] Ibid., p.316 (PLBA, 252).

[85] See, for example, Pr.Ch., R-8 (1906) 624 (PLBA, 335); and the footnotes to tables 57 (P30) and 63 (P36).

Pt = 198, Ir = approximately 197, Os = approximately 196 - 195, and Au = ca.199".[86] Over the next few years Mendeleev's prediction on the basis of the periodic system regarding the order of increase of the atomic weights of Os, Ir, Pt and Au was confirmed by the results of various investigators. This success of the periodic system was pointed out by Mendeleev in his Faraday Lecture of 1889:

> ... the expectations of the periodic law have been brilliantly confirmed in respect of the series Os, Ir, Pt, Au, in which an increase in atomic weight was to be expected,[87] but where at the time of the appearance of the periodic law the numbers given by Berzelius, Rose and others were the following: Os = 200; Ir = 197; Pt = 198; Au = 196. Justification of the expectations of the periodic law has been provided first by the new determinations (by Seubert, Dittmar and M'Arthur) of the atomic weight of platinum, which proved to be close to 196 (taking O = 16, as proposed by Marignac, Brauner and others); secondly by the fact that Seubert showed that the atomic weight of osmium is in fact lower than that of platinum, and close to Os = 191; and thirdly by the fact that for gold, as a result of the researches of Krüss, Thorpe and Laurie, there is now no doubt that its atomic weight is greater than that of platinum, being approximately 197 (if O = 16).[88]

d) Cobalt and nickel

The pair of elements Co and Ni, like the pair Te and I, shows a decrease of atomic weight with increase in atomic number, the modern atomic-weight values being Co = 58.9, Ni = 58.7 (O = 16). Mendeleev had finally placed these elements in the correct order in his periodic table, with Co preceding Ni, by the end of 1870 (see Fig. III-20);[89] but there was not yet any problem of atomic-weight inversion because the currently-accepted atomic-weight values, which Mendeleev adopted, were the same for both elements, viz. Co = Ni = 59 (H = 1). It was not until the 1880's that atomic-weight determinations came to indicate a smaller value for Ni than for Co, e.g. Zimmerman in 1886 found Co = 58.74, Ni = 58.56 (H = 1).[90]

Mendeleev continued to take the atomic weights of Co and Ni as being the same until 1881. From 1881 to 1895 he tended to assign a slightly lower atomic weight to Co than to Ni, in accordance with the demands of atomic-weight

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[86] Op.cit., p.211 (PLBA, 161).

[87] Mendeleev here appends a footnote referring to his prediction in The periodic lawfulness of the chemical elements (G.; 1871) concerning the order of increase of atomic weights in the series Os, Ir, Pt, Au.

[88] PLBA, 229-30.

[89] Odling had placed Fe, Co and Ni in the correct order in his table of 1864 (see Fig. III-6).

[90] Zimmerman, Annalen, 232 (1886) 324.

ordering in the periodic table, e.g. see tables 47 (1881), 52 (1889) and 55 (1895). There was no real empirical justification for this (in fact the evidence pointed increasingly to the opposite atomic-weight order), although after 1886 a spurious justification was presented by Mendeleev through suitable selection of empirical data, by taking Zimmerman's value of 58.5 for Co and Winkler's earlier value of 59 for Ni (as indicated above, Zimmerman's value for Ni was greater than for Co).[91] After 1895 Mendeleev no longer assigned a lower atomic-weight value to Co than to Ni.

The atomic-weight inversion for Co and Ni which was indicated by the experimental results of the 1880's presented rather less of a problem for the periodic system than had the case of Te and I - not only because for Co and Ni the atomic-weight difference was smaller, and hence the apparent inversion more readily attributable to experimental error in the atomic-weight determinations, but also because the order demanded in the periodic table on the grounds of chemical analogy was less clear-cut in the case of Co and Ni than in the case of Te and I, it being not impossible that a more detailed study of chemical properties might support the ordering Fe, Ni, Co, Cu rather than Fe, Co, Ni, Cu. Thus Mendeleev in 1898, in an article entitled The periodic lawfulness of the chemical elements (R.) in which he listed the atomic weights as Co = 58.93 and Ni = 58.69 (O = 16), commented:

> The periodic law gives grounds for maintaining that the atomic weight of cobalt is less than that of nickel, but the majority of existing determinations, while indicating that the atomic weights of Co and Ni are very close, have so far nevertheless forced us to assign to cobalt a slightly greater atomic weight than to nickel. We may suppose, however, that the methods of separation and the means of determining composition have so far been insufficiently precise, and that more precise determinations will give a smaller weight for Co than for Ni.[92]
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> There are many grounds for supposing that of the similar elements Co and Ni, the former is closer to iron, and the latter to copper, i.e. that the series according to increasing atomic weight is Fe, Co, Ni, Cu ... But the majority of existing data nevertheless support a greater atomic weight for Co than for Ni, and therefore it is desirable that new determinations, as precise as possible, should decide this question finally be means of comparative and parallel experiments for Ni and Co. If it be shown by such determinations that Co is heavier than Ni, i.e. that the series must be written Fe, Ni, Co, Cu, then further

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[91] See, for example, Mendeleev's article on The weight of atoms (R.) in Bibl.11, vol. 7, half-vol. 14, 1892, 658-660; p.660 (PLBA, 412).

[92] Bibl.11, vol. 23, half-vol. 45, 1898, p.316 (PLBA, 251).

> investigations of the analogies of Co and Ni with Rh and Pd, and with Ir and Pt, would be desirable, in connection with which the complex double salts and compounds like $Ni(CO)_4$ would be particularly important.[93]

It seems to have been in the spirit of the second of these passages (i.e. acknowledging that perhaps Ni might be placed before Co in the periodic table), rather than as an acceptance of the possibility of an atomic-weight inversion in the periodic table, that Mendeleev wrote in the 7th (1902-3) and 8th (1906) editions of Principles of Chemistry, "But even if it be shown without doubt that the atomic weight of Ni is greater than that of Co, the essence of the periodic law would in no way be disturbed, especially as the matter concerns group VIII where the highest saline oxides are variable in composition and do not possess sharply distinctive properties".[94]

The atomic-weight values given to Co and Ni in Mendeleev's periodic tables of the early 20th century were those which he had used before 1881, viz. Co = 59, Ni = 59. In tables 57 (P30) and 63 (P36), from the 7th and 8th editions of Principles of Chemistry respectively, the following footnote was appended to the entry "Co = 59, Ni = 59":

> An atomic weight of 58.7 is found for Ni, but because this metal, judging from its properties, should follow Co = 59, we must expect for it an atomic weight greater than that of Co, not smaller; and therefore with further investigations we can expect a certain (slight) change in atomic-weight value for Co and Ni.

e) Argon and potassium

Mendeleev adopted the placing of argon between Cl and K in the periodic table early in the 20th century (see Ch.VII, section C). He included argon in his periodic tables as Ar = 38, although vapour-density measurements indicated an atomic weight of 39.9. He assumed the lower value solely for the sake of regular atomic-weight ordering in the sequence Cl (35.5), Ar, K (39.1). On this matter he wrote in the 7th (1902-3) and 8th (1906) editions of Principles of Chemistry: "The density of argon indicates an atomic weight of 39.9, but ... we must think that the atomic weight of Ar is greater than that of Cl, but lower than that of K, i.e. about 38".[95] Mendeleev's view that the atomic weight of argon would in fact prove to be lower than that of potassium has not been vindicated. Like Te - I and Co - Ni, the pair of elements Ar - K shows a decrease of atomic weight with increase in atomic number.

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[93] Ibid., pp.321-2 (PLBA, 268-9).

[94] For example, Pr.Ch., R-8 (1906) 624 (PLBA, 335).

[95] This remark is given in a footnote to tables 57 (P30) and 63 (P36).

C. Mendeleev's use of the periodic system for the prediction of the existence and properties of unknown elements.[96]

1. Mendeleev's prediction of the existence and properties of the three elements "eka-boron" (scandium), "eka-aluminium" (gallium) and "eka-silicon" (germanium).[97]

In the article Correlation of properties (R.; 1869) Mendeleev concluded, on the basis of gaps in his "attempt at a system", that "We must expect the discovery of many yet unknown elements, e.g. elements analogous to Al and Si, with atomic weights 65-75".[98] The "attempt at a system" itself (the manuscript table 3, and the published tables 8 and 9) contains a prediction of these unknown analogues of Al and Si in the form of the entries "? = 68" and "? = 70" in the rows containing Al and Si respectively, between Zn = 65.2 and As = 75 in the fourth column. The predicted elements "? = 68" and "? = 70" correspond according to their atomic weights and position in the "attempt at a system" to the then unknown elements gallium (= 69.2) and germanium (= 72.0) respectively. Also in Mendeleev's "attempt at a system" of 1869 is the entry "? = 45". Although corresponding according to atomic weight to the unknown scandium (= 44.6), this predicted element "? = 45" does not show a close correspondence to scandium in its placing in the "attempt at a system": admittedly "? = 45" follows immediately after Ca in this table, as should Sc, but the particular (unsatisfactory) arrangement of elements in the "attempt at a system" is such that "? = 45" is followed by Er = 56, and its only listed analogue (in the same horizontal row) is Ce = 92. Thus whereas Mendeleev can reasonably be considered to have already predicted the existence and atomic-weight values of Ga and Ge in his first published periodic table (i.e. in table 8), it is doubtful whether there is sufficient justification for recognising also a similar prediction of Sc in this table.[99]

The earliest publication by Mendeleev of what can be definitely recognised as a prediction of the existence of scandium is seen in table 10 (P3), in the

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[96] Also considered in this section are certain predictions made by Mendeleev concerning known elements - notably certain additional predictions of properties for gallium (= "eka-aluminium") which were made after he had learned of the discovery of this element, and predictions of the properties of an element which he called "dvi-boron" but which was in fact the known element yttrium.

[97] Mendeleev's predictions concerning "eka-boron", "eka-aluminium" and "eka-silicon" are considered here in a separate sub-section from his predictions concerning other unknown elements because of their greater detail and because of their special significance for the consolidation of the periodic law.

[98] Op.cit., p.76 (PLBA, 31).

[99] Spronsen holds a similar view (see Bibl.110, p.220); Kedrov, on the other hand, does recognise the entry "? = 45" in tables 8 (P1) and 9 (P2) as corresponding to a prediction of scandium (see, for example, Sc.Ar., 826).

form of a dash included between Ca and Ti representing an unknown analogue of B and Al. Table 10 (P3) was published in Correlation of properties together with table 9 (P2); but whereas the entry "? = 45" in the long-form table 9 (P2) cannot conclusively be identified with scandium, the short-form table 10 (P3) has an unoccupied place which corresponds clearly to that of scandium in the modern periodic table. It was not until early 1871 that Mendeleev published a prediction not merely of the existence but also of the atomic-weight value of an unknown element which can reasonably be identified with scandium, suggesting the value 44 (see, for example, table 30). However, a study of the manuscript periodic tables drawn up by Mendeleev shows that he had already committed to paper an atomic-weight value (of 45) for an unknown element corresponding to scandium as early as March 1869, in the short-form table 6 (M6).

In the summer of 1869 Mendeleev drew up a manuscript partial periodic table, table 12 (M9), listing the atomic volumes of certain elements. He marked two gaps between Zn (atomic volume given as 9.1) and As (at.vol. 13) corresponding to the places of Ga and Ge, but did not include values for these missing elements.[100] Two months later, in his paper on Atomic volumes which he read to the Moscow Congress of Russian Scientists and Physicians, he suggested that "those two elements which are still missing from the system and which show a resemblance to Al and Si, and have atomic weights of about 70, will have atomic volumes of about 10 or 15, i.e. will have specific gravities of about 6";[101] he thought at this stage that the lighter (according to atomic weight) of these two elements, i.e. the analogue of aluminium, might perhaps be indium.[102] In the manuscript table 19 (M13), dating from the summer-early autumn of 1870, Mendeleev listed the atomic volumes of the unknown elements corresponding to Sc, Ga and Ge as 15, 11.5 and 13 respectively.

During the second half of 1870 Mendeleev is known to have drawn up a number of manuscript periodic tables containing atomic-weight values for unknown elements corresponding to Sc, Ga and Ge. In table 16 (M10) the values given were 44, 68 and 74 respectively; in table 17 (M11) they were 45, 68 and 72; subsequent manuscript tables of 1870 - notably tables 20 (M14),

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[100] Table 12 (M9) does not include the row which would contain Sc.

[101] Op.cit., p.67 (PLBA, 42).

[102] Ibid. (see earlier in the present chapter, p.337).

23 (M16), 24 (M17), 25 (M18), 26 (M19) - consistently gave 44, 68 and 72, which are the values to be found also in Mendeleev's published tables of 1871 and later for these unknown elements.

Table 26 (M19) was the manuscript version of table 30 (P7), the table published early in 1871 in the article A natural system of the elements (R.). This article A natural system of the elements was the earliest published source of Mendeleev's detailed predictions of the properties of the unknown elements corresponding to Sc, Ga and Ge, for which unknown elements he now introduced the labels "eka-boron", "eka-aluminium" and "eka-silicon" respectively.[103] In this article Mendeleev showed an especially great interest in "eka-silicon" - "it seems to me that the most interesting of the undoubtedly missing metals will be ... eka-silicon".[104] It is not clear why "eka-silicon" should have appeared more interesting to Mendeleev than "eka-boron" or "eka-aluminium", but it was perhaps partly because he linked this element with what he saw as the problem of the irregularly high atomic-weight value Ti = 50 (see section B, sub-section 2, of the present chapter). Mendeleev seems to have considered the discovery of "eka-silicon" to have been more imminent than that of "eka-boron" or "eka-aluminium". In fact during the early part of 1871 he felt that perhaps the new element "ilmenium" which the Moscow chemist Hermann claimed to have discovered in the mineral ilmenite ($FeTeO_3$) was actually "eka-silicon";[105] by mid-1871, however, he had rejected the authenticity of "ilmenium" as an element, as had most chemists.[106] Towards the end of 1871 Mendeleev set out to search for "eka-silicon" himself. He obtained samples of various titanium minerals (including ilmenite) in which he hoped to find the missing element, but very soon gave up the arduous search, shifting his attention in December 1871 to the completely different field of the study of the elasticity of gases.

In November 1871 Mendeleev's article on The periodic lawfulness of the chemical elements (G.) was published, containing a section headed "On the application of the periodic law to the determination of the properties of

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[103] Also in this article Mendeleev made a number of less detailed predictions concerning other unknown elements (see later).

[104] Op.cit., pp. 49-50 (PLBA, 95).

[105] See, for example, A natural system of the elements (R.; 1871), p.53, footnote (PLBA, 98); and also table 31 (P8).

[106] See The periodic lawfulness of the chemical elements (G.; 1871), p.204 (PLBA, 156).

elements as yet undiscovered".[107] Here Mendeleev again gave detailed predictions of the properties of "eka-boron", "eka-aluminium" and "eka-silicon".[108] Two years later (1873) his predicted properties for "eka-silicon" were published in the 2nd edition of Principles of Chemistry,[109] as they were also in all subsequent editions of this work (i.e. including those editions published after the discovery of germanium in 1886).[110]

In August 1875 the presence of a hitherto unknown element in zinc blende from Pierrefitte in the Pyrenees was recognised by Lecoq de Boisbaudran, who gave this new element the name "gallium". De Boisbaudran initially identified gallium as a new element by means of its characteristic spectrum, not having sufficient material to separate it from the accompanying zinc. He determined certain of its chemical properties, a relatively large quantity of zinc being present in the reactions studied. De Boisbaudran's report of his discovery was published in the Comptes Rendus in September 1875;[111] a report appeared in Russian in the following month.[112] Having learned of de Boisbaudran's discovery (presumably from the Russian report) Mendeleev immediately sent a note to the Comptes Rendus pointing out that the few properties so far determined for gallium suggested that this new element was in fact none other than the "eka-aluminium" which he himself had predicted in 1870-71. In this note, which was published in November 1875,[113] Mendeleev again presented various predictions regarding the properties of "eka-aluminium", most of which he had already given earlier, but with a few additional ones.[114] Later in 1875, and in 1876, de Boisbaudran further investigated the properties of gallium;[115] in 1876 he managed to isolate free metallic gallium for the first time (in very small quantities).

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[107] Op.cit., pp. 196-206 (PLBA, 150-7).

[108] At the same time he mentioned also various other unknown elements whose existence he foresaw on the basis of gaps in the periodic table (see later).

[109] Pr.Ch., R-2, part II (1873) 756 (PLSM, 312-3).

[110] See, for example, Pr.Ch., R-8 (1906) 257 (PLBA, 294-5).

[111] Caractères chimiques et spectroscopiques d'un nouveau métal, le Gallium, découvert dans une blende de la mine de Pierrefitte, vallée d'Argelès (Pyrénées). Note de M. Lecoq de Boisbaudran, présentée par M. Wurtz. Comptes Rendus, 81 (1875) 493-5.

[112] J.Russ.Phys.Soc. and Chem.Soc., 7 (1875) no. 8, chem. part, section 2, p.405. This was a report of de Boisbaudran's Comptes Rendus publication, sent to Petersburg by de Clairmont.

[113] Remarques à propos de la découverte du Gallium, Comptes Rendus, 81 (1875) 969-72 (Russian translation: PLBA, 198-202).

[114] Also in this note Mendeleev drew attention to the applicability of the periodic law to the correction of the atomic-weight values of known elements (see earlier in the present chapter, p. 341).

[115] Comptes Rendus, 81 (1875) 1100-1105; 82 (1876 168, 1036-1039; 83 (1876) 611-3.

In 1879 Nilson discovered a new element in the rare-earth mineral gadolinite; he named this element "scandium".[116] The identity of scandium with Mendeleev's "eka-boron" was soon pointed out by Clève.[117]

Seven years later (1886) Winkler discovered a new element, which he named "germanium", in the silver ore argyrodite.[118] Winkler at first thought that germanium was an analogue of Sb, occupying the empty place between Sb and Bi in Mendeleev's periodic table (i.e. the place V-9, which would require an atomic weight for germanium of ca. 165);[119] but before the end of 1886 a fuller study of its properties had shown it to be Mendeleev's "eka-silicon", with an atomic weight of ca. 72.

The following three tables a), b) and c) present a comparison of the properties predicted by Mendeleev for the elements "eka-aluminium", "eka-boron" and "eka-silicon" with those actually found for gallium, scandium and germanium.[120] Mendeleev's predictions are taken from four sources: his articles A natural system of the elements (R.) and The periodic lawfulness of the elements (G.) published in 1871, the 2nd edition (1873) of Principles of Chemistry (R.), and his Note in connection with the discovery of gallium (F.) of 1875.[121] Because Mendeleev's predictions of 1875 for "eka-aluminium" were made after he had become acquainted with de Boisbaudran's initial note on gallium, the new predictions which he gave at this time have been distinguished in table a) from his earlier predictions regarding this element: only very few of Mendeleev's new predictions of 1875 for "eka-aluminium" could possibly be regarded as having been "unfair" in the sense of his having had prior knowledge of their correctness, since not many properties had yet been ascertained for gallium,

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[116] Comptes Rendus, 88 (1879) 645-8; Berichte, 12 (1879) 554-7.

[117] Comptes Rendus, 89 (1879) 419-22; Chem. News, 40 (1879) 159-60.

[118] Berichte, 19 (1886) 210-11.

[119] Ibid., p.211.

[120] Various similar, but less comprehensive, tables have been given elsewhere, e.g. J.W. Mellor, A comprehensive treatise on inorganic and theoretical chemistry, vol. I (1922) p.261 (Ge), vol. V (1924) pp.373 (Ga) and 480 (Sc); Weeks and Leicester, Bibl. 130, pp. 647 (Ga), 652 (Sc) and 661 (Ge); and Spronsen, Bibl. 110, p.139.

[121] The symbols used by Mendeleev for "eka-boron" and "eka-silicon" were "Eb" and "Es" respectively; for "eka-aluminium" he used "El" in A natural system of the elements (1871) and in his Note in connection with the discovery of gallium (1875), and "Ea" in The periodic lawfulness of the chemical elements (1871).

but one such new "prediction" which certainly seems to have been unfair in this respect was that of the tendency for "eka-aluminium" oxide to be precipitated from aqueous solutions of "eka-aluminium" salts by $BaCO_3$, a property which, as Mendeleev knew, had already been reported for gallium by de Boisbaudran.[122]

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[122]Mendeleev explicitly acknowledged de Boisbaudran's observation of such precipitation of gallium by $BaCO_3$, in his Note in connection with the discovery of gallium (F.), p.971 (PLBA, 202).

a) A comparison of the properties predicted by Mendeleev for "eka-aluminium", and those actually found for gallium.

Eka-aluminium, El or Ea	Gallium, Ga
General character: Properties should represent a mean of those of Zn and eka-silison on the one hand, and those of Al and In on the other. More acidic than eka-boron.	Many properties represent a transition from those of Zn to those of Ge on the one hand, and from those of Al to those of In on the other. More acidic than scandium.
Atomic weight: ca. 68 (H=1).	69.2 (H=1).
Free element: A metal, which should be fairly easily obtained by reduction using C or Na. Its properties should in all respects represent a transition from those of metallic Al to those of metallic In, e.g. it will be more volatile than metallic Al, less so than metallic In. Sp.grav., ca. 6.0 (atomic vol., ca. 11.5). [1875: Metal easily obtained by reduction. Sp.grav., 5.9. Will melt at quite a low temperature. Almost involatile. Not oxidised on contact with air. When heated to red-heat, should decompose water. The pure and fused metal will be only slowly subject to the action of acids and bases.]	A metal; can be prepared by heating the oxide in hydrogen, or from aqueous solution by electrolysis. Sp.grav., 5.9 (atomic vol., 11.8). Melting-pt., 29.78°C (this is lower than that of both In, 157°C, and Al, 660°C). Boiling-pt. is high, probably above 2,000°C; it probably falls between that of Al and that of In, but recorded figures are so discordant that this cannot be claimed with certainty. The metal is not oxidised in air at ordinary temperatures. Action on steam unknown. Gallium metal dissolves slowly in acids and alkalis.
Oxides and hydroxides: Formula of oxide, Ea_2O_3. The hydrous oxide will dissolve in KOH solution. Manuscript table 34 (M21), early summer 1871, gives specific vol. of oxide as "33?". [1875: Sp.grav. of oxide, ca. 5.5. Basic properties more	The stable oxide is Ga_2O_3, gallic oxide. This is soluble in HCl, H_2SO_4, and aqueous alkali hydroxide and ammonia; but if it has been previously strongly heated it dissolves in these media only extremely slowly. Barium carbonate precipitates

(Properties of eka-aluminium/gallium, continued)

distinct than for Al_2O_3, less than for ZnO; we should therefore expect it to be precipitated by $BaCO_3$. Soluble in strong acids. Should form an amorphous hydrate which is insoluble in water, but which dissolves in acids and alkalis.]

Halides: Should give a volatile anhydrous chloride, which is more stables than aluminium chloride.

[1875: $ElCl_3$ will be more volatile than $ZnCl_2$.]

Other compounds: The salts of eka-aluminium will be more stable than aluminium salts.

Eka-aluminium will certainly form alums.

Its sulphide, Ea_2S_3, will be insoluble in water, and will probably be precipitated by ammonium sulphide.

It should give volatile organo-metallic compounds.

[1875: Eka-aluminium will form neutral and basic salts $El_2(OH,X)_6$, but not acid salts.

The alum $ElK(SO_4)_2.12H_2O$ will be more soluble than the corresponding aluminium salt, and have less tendency to crystallise.

The sulphide El_2S_3 or oxysulphide $El_2(S,O)_3$ should be precipitated by H_2S and will be insoluble in ammonium sulphide.]

the hydroxide from aqueous solutions of gallium salts. The hydroxide dissolves in aqueous acids and alkalis.

sp. gravity of oxide

Anhydrous gallic chloride fumes in moist air; it is hydrolysed by water with a hissing sound, though less violently than is aluminium chloride. Boiling-pt., 200°C ($ZnCl_2$ boils at 730°C).

Gallic salts are even more strongly hydrolysed in solution than are those of aluminium.

Gallium forms alums.

Ga_2S_3 is not precipitated by H_2S or $(NH_4)_2S$ in the absence from the solution of other metals. It is, however, almost quantitatively carried down with a number of other metallic sulphides (e.g. ZnS) when they are precipitated from alkaline or acetic acid solutions by H_2S. It is similarly precipitated with ZnS and other metallic sulphides by $(NH_4)_2S$.

Gallium forms a basic sulphate in addition to the neutral sulphate. It does not form acid salts.

Gallium gives volatile organo-metallic compounds.

(Properties of eka-aluminium/gallium, continued)

Points relating to discovery: Eka-aluminium is likely to be discovered spectroscopically (on the grounds of its expected degree of volatility), like In and Tl.	Gallium was discovered spectroscopically.

b) A comparison of the properties predicted by Mendeleev for "eka-boron", and those actually found for scandium.

Eka-boron, Eb	Scandium, Sc.
General character: Should be more basic in character than are B and Al.	Is more basic in character than are B and Al.
Atomic weight: 44 (H=1). (Mendeleev also suggested 45, but clearly preferred 44).	44.6 (H=1).
Free element: A metal; sp.grav. ca. 3.0 (probably a little higher), i.e. atomic vol. ca. 15. Will be involatile, and not easily fusible. Will not decompose water at ordinary temperatures; at elevated temperatures it should do so, but only partially and with difficulty (giving Eb_2O_3). Will certainly dissolve in acids, H_2 being given off.	A metal; sp.grav. 3.1, melting-pt. 1,400°C. Little is known about the properties of metallic scandium because of the difficulty of preparation of the pure metal.
Oxides and hydroxides: Oxide, Eb_2O_3, will have sp.grav. of ca. 3.5 (sp.vol. ca. 39). Infusible, involatile powder. Less basic than MgO and yttria, more basic than alumina. Will be only very weakly water-soluble; will probably give water an alkaline reaction to litmus. Soluble in acids, with which it should form stable salts. Will probably not form stable compounds (undecomposed by water) with alkalis. It will certainly not dissolve in ammonia, but it is possible (though not likely) that it will dissolve weakly in KOH solution. Unlikely to extract NH_3 from NH_4Cl.	Oxide, Sc_2O_3; pyknometric measurements give sp.grav. 3.86, X-ray measurements give 3.1. Sc_2O_3 is more basic than Al_2O_3, less basic than MgO and yttria. Ignited scandia dissolves with difficulty in cold dilute acids, but readily in warm acids (especially when the latter are concentrated). It is not soluble in alkalis, and only negligibly so in water. It does not decompose NH_4Cl.

(Properties of eka-boron/scandium, continued)

Halides: Eka-boron chloride will be a solid, salt-like anhydrous substance. Its degree of volatility will depend upon whether it has the molecular formula $EbCl_3$ (more volatile) or Eb_2Cl_6 (less volatile), but its volatility is probably less than that of aluminium chloride. It will be hygroscopic. Will be decomposed by water, giving HCl, more readily than is $MgCl_2$; but it will not have the character of a chloroanhydride. Sp.vol. is probably ca. 78, i.e. sp.grav. (for the formula $EbCl_3$) ca. 2.0.	Scandium chloride, $ScCl_3$, is a white deliquescent solid; much less volatile than aluminium chloride. Is hydrolysed in aqueous solution. Sp.grav. of anhydrous $ScCl_3$ is 2.39.
Other compounds: Salts will be colourless, and will give gelatinous precipitates with KOH, K_2CO_3, Na_2HPO_4. Only a few salts will crystallise well, and these will be double salts. The sulphate will be less soluble than $Al_2(SO_4)_3$. Eka-boron will show little tendency to form alums. It will form a double sulphate with K_2SO_4, but this will not be isomorphous with the alums. The carbonate will be insoluble in water, precipitating as a basic salt. Eka-boron will not form organometallic compounds.	Scandium salts are colourless. The carbonate and phosphate are insoluble in both water and alkalis. The carbonate readily loses CO_2. Scandium sulphate is readily soluble, more so than $Al_2(SO_4)_3$; it crystallises with difficulty. It is not very soluble in sulphuric acid. It forms double sulphates which are not isomorphous with alums. Scandium does not seem to give organometallic compounds.
Points relating to discovery: Because of the probable involatility of the metal, eka-boron is unlikely to be discovered by means of spectral analysis. (A natural system of the elements, R., 1871).	Scandium was not discovered by means of spectral analysis.

(Properties of eka-boron/scandium, continued)

Although the salts of eka-boron will have low volatility, they may still be volatile enough for the element to be discovered spectroscopically. (Annalen, 1871).	

c) A comparison of the properties predicted by Mendeleev for "eka-silicon", and those actually found for germanium.

Eka-silicon, Es	Germanium, Ge
General character: Properties should represent a mean of those of eka-aluminium and As on the one hand, and of Si and Sn on the other. Will be more acidic in its properties than Ti. Will show little tendency to give a lower oxidation state (i.e. lower than 4).	Many properties of Ge represent a transition from those of Ga to those of As on the one hand, and from those of Si to those of Sn on the other. Ge is more acidic than Ti. Ge (II) compounds are unstable, tending to be oxidised to Ge (IV).
Atomic weight: ca. 72 (H=1).	72.0 (H=1).
Free element: Dark grey metal. Fusible (A natural system of the elements, R., 1871); fusible with difficulty (Annalen, 1871); refractory (Pr.Ch., R-2, 1873). Sp.vol. ca 13 (1871), ca.10 (1873); sp.grav. ca 5.5. Volatile under strong heat. Oxidised by calcination, giving EsO_2. Will perhaps decompose steam, but with difficulty. Acids will act on it only very weakly, but alkalis more readily. Should be easily prepared by reduction of K_2EsF_6 by Na, or of EsO_2 by C.	Greyish-white metal; sp.grav. 5.35 (20°C). Melting-pt. 958°C; boiling-pt. is high, ca. 2,000°C. Ge burns with incandescence when heated in oxygen, giving GeO_2; in air, at red-heat the metal becomes covered with a thin layer of oxide. Ge does not decompose water. It is not attacked by hydrochloric acid, but is by aqua regia. KOH solutions have no action, but fused KOH oxidises it. Is prepared by reduction of K_2GeF_6 by Na, or of GeO_2 by C.
Oxides and hydroxides: Oxide, EsO_2, will be a refractory powder; sp.grav. ca. 4.7 (sp.vol. ca. 22). In its appearance - even perhaps in crystalline form - and in its properties and reactions it will resemble TiO_2. Its general character will be that of a weak but distinct acid, more acidic than TiO_2. As a base it will be	The oxide GeO_2 is refractory, and has a sp.grav. of 4.70. The acidic character of GeO_2 considerably outweighs its basic character. If GeO_2 is prepared by hydrolysis (e.g. of $GeCl_4$) it is produced as a gelatinous hydrate. Acids do not precipitate the hydrate from dilute alkaline solutions;

(Properties of eka-silicon/germanium, continued)

weaker than TiO_2 and SnO_2, but stronger than SiO_2. Should give a gelatinous hydrate which is soluble in acids, although such solutions will readily decompose to give a metahydrate which is insoluble in acids. All hydrated forms will be soluble in alkalis.	but from concentrated solutions acids precipitate GeO_2 or a metahydrate.
Halides: Volatile anhydrous chloride, $EsCl_4$; boiling-pt. ca. 90°C (A natural system of the elements, R., 1871), ca. 100°C (probably somewhat less) (Annalen, 1871), ca. 100°C (Pr.Ch., R-2, 1873). Sp.grav. ca 1.9 at 0°C; sp.vol. ca. 113. Will be an acid chloroanhydride, decomposed by water. EsF_4 probably not gaseous.	$GeCl_4$ boils at 83°C, and has a sp.grav. of 1.88 (18°C). It is slowly hydrolysed by water, giving a gel of hydrated GeO_2. $GeF_4 \cdot 3H_2O$ is a white solid, which hydrolyses upon attempt at dehydration by heating.
Other compounds: Will form salts of low stability. Will form K_2EsF_6, isomorphous with the corresponding compounds of Si, T, Zr, Sn. Will give volatile organometallic compounds. $EsEt_4$ will have a boiling-pt. of ca. 160°C, and a sp.grav. of ca. 0.96. EsH_4 expected to be formed, but probably easily decomposable. The sulphide, EsS_2 will be insoluble in water, but will probably give solutions with $(NH_4)_2S$.	$Ge(SO_4)_2$ is hydrolysed by water. Thermal decomposition sets in at ca. 200°C. Forms K_2GeF_6 and $(NH_4)_2GeF_6$, isomorphous with the corresponding fluorosilicates. $GeEt_4$ boils at 160°C, and has a sp.grav. slightly lower than that of water, 0.991. Ge also forms other alkyls. Forms GeH_4, which is decomposed on heating. GeS_2 shows only slight solubility in water, but is readily soluble in $(NH_4)_2S$ solution.

(Properties of eka-silicon/germanium, continued)

Points relating to discovery: Will probably be discovered in association with Ti, Zr or Nb; most likely source is with Ti minerals. (1871). Es should be looked for in association with As and Ti (1875: Remarques à propos de la découverte du gallium).	Ge was found in the silver ore, argyrodite - $GeS_2.4Ag_2S$.

Comparison of the properties predicted by Mendeleev for the unknown elements "eka-aluminium", "eka-boron" and "eka-silicon" with those actually found for gallium, scandium and germanium shows a remarkable degree of agreement for the majority of properties; indeed, the correspondence of predicted and observed properties is such that Mendeleev, in 1889 and later, felt justified in claiming that his predictions for "eka-aluminium", "eka-boron" and "eka-silicon" had been "completely confirmed".[123] However, there are in fact a few instances where predictions made by Mendeleev for these elements have turned out not to be correct:-

i) Mendeleev predicted in 1871 that the properties of metallic "eka-aluminium" should "in all respects" represent a transition from those of metallic aluminium to those of metallic indium;[124] yet the melting-point of gallium metal (30°C) is actually appreciably lower than that of either Al (660°C) or In (155°C). Admittedly in 1875 Mendeleev predicted that "eka-aluminium" should melt at a "fairly low temperature",[125] but there is no indication that by this he meant a temperature lower than the melting-point of indium.

ii) Mendeleev claimed that the salts of "eka-aluminium" will be "more stable (postoiannee)" than aluminium salts;[126] yet gallic salts are even more strongly hydrolysed in solution than are those of aluminium. (Of course, resistance to hydrolysis is only one aspect of "stability").

iii) Mendeleev predicted that Ea_2S_3 would be precipitated from aqueous solutions of Ea salts by H_2S or $(NH_4)_2S$;[127] but this is the case for Ga_2S_3 only under special conditions, if zinc or certain other metals are also present in the solution.

iv) Mendeleev predicted that "eka-boron" sulphate would be less soluble than $Al_2(SO_4)_3$.[128] Scandium sulphate is actually more soluble than $Al_2(SO_4)_3$.

v) In his Annalen paper of 1871, and in the 2nd edition of Principles of Chemistry (1873), Mendeleev predicted that metallic "eka-silicon" would be

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[123] Faraday Lecture, 1889: PLBA, 225. The periodic lawfulness of the chemical elements (R.), 1898, p.320 (PLBA, 263).

[124] A natural system of the chemical elements (R.), p.47 (PLBA, 92).

[125] Note in connection with the discovery of gallium (F.), p.971 (PLBA, 201).

[126] A natural system of the chemical elements (R.), 1871, p.47 (PLBA, 92).

[127] The periodic lawfulness of the chemical elements (G.), 1871, p.200 (PLBA, 153); Note in connection with the discovery of gallium (F.), 1875, p.970 (PLBA, 201).

[128] The periodic lawfulness of the chemical elements (G.), 1871, p.198 (PLBA, 151).

a refractory substance.[129] In fact Ge melts at about 950°C, not an especially high temperature for the melting-point of a metal.

Of these incorrect predictions it seems that those referred to in ii), iii) and iv) were not appreciated as being incorrect during Mendeleev's time - at least, certainly not by Mendeleev himself. The prediction mentioned in iii) was in fact probably considered to be perfectly correct, because of its agreement with the observed precipitation of Ga_2S_3 with ZnS when zinc is present in solution with the gallium. As regards the prediction, referred to in v), that metallic "eka-silicon" should be refractory, Mendeleev certainly knew by 1889 that the melting-point of Ge is ca. 900°C[130]; but he does not appear to have discussed this value in relation to his prediction. On the question of the exceptionally low melting-point observed for gallium, mentioned above in i), Mendeleev (1879) gave the following post hoc rationalisation of this low value:

> ... we should pay heed to the fact that the melting-point of gallium is so low that it melts at the temperature of the hand. It might appear that this property is unexpected; but this is not so. It suffices to look at the following series -
>
> | | | | | | |
> |---|---|---|---|---|---|
> | Mg | Al | Si | P | S | Cl |
> | Zn | Ga | ... | As | Se | Br |
> | Cd | In | Sn | Sb | Te | J. |
>
> It is evident that in the group Mg, Zn, Cd, the most refractory metal has the lowest atomic weight; but in the groups beginning with S and Cl, the most difficultly fusible simple bodies are, on the contrary, the heaviest. In a transitionary group, such as Al, Ga, In, we must expect an intermediate phenomenon; the two extreme elements, the heaviest (In) and the lightest (Al), should be less fusible than the middle one, which is as it is in reality. I turn attention to the fact that properties such as the melting-point of bodies depend chiefly upon molecular weight, and not atomic weight. If we were to have a variety of solid sulphur not in the form of S_6 (or, perhaps, of still heavier molecules S_n), but in the form S_2, which it assumes at 800°C, then its temperature of melting and of boiling would undoubtedly be very much lower. In just the same way, ozone, O_3, condenses and solidifies much more readily than does ordinary oxygen, O_2.[131]

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[129] Ibid., p.201 (PLBA, 153); Pr.Ch., R-2, part II (1873) 756 (PLSM,313). In A natural system of the elements (R.; 1871), p.50 (PLBA, 95) Mendeleev had said that "eka-silicon ... will in any case be a fusible metal".

[130] See, for example, Pr.Ch., R-5 (1889) 537-8 (PLSM, 386).

[131] Le Moniteur Scientifique [3], 9 (1879) 692 (PLBA, 393-4).

This particular argument on the basis of the trends in the periodic system in support of a lower melting-point for gallium than for either indium or aluminium had not been given by Mendeleev before the melting-point of gallium was determined; and in fact it is not at all in the spirit of the method of simple interpolation from the properties of "atomanalogues" (closest vertical and horizontal neighbours in the periodic system) which he had originally used for predicting the properties of the unknown "eka"-elements.

Of the many successful predictions made by Mendeleev regarding the properties of "eka-aluminium", "eka-boron" and "eka-silicon", that of the specific gravity of metallic "eka-aluminium" is perhaps of special interest, because of the particular story of its confirmation. De Boisbaudran in 1876 had obtained a value of 4.7 for the specific gravity of metallic gallium,[132] which did not at all agree with Mendeleev's prediction of a specific gravity of ca. 6.0 for metallic "eka-aluminium". Because agreement between the other properties so far found for gallium and those predicted by Mendeleev for "eka-aluminium" had in general turned out to be very good, de Boisbaudran soon set about re-determining the specific gravity of gallium. He discovered that the gallium used in his original determination had been contaminated with an appreciable amount of metallic sodium (sp.gr. 0.98; sodium had been used as reducing agent in the isolation of free gallium metal), and he now obtained a value of ca. 5.95 (at 25°C) for the specific gravity of purified gallium, agreeing well with Mendeleev's prediction for "eka-aluminium".[133] Concerning this matter Mendeleev wrote in 1898:

> If it had not been for the indications of the periodic law it would have been thought for a long time that gallium has a specific gravity of 4.7, as was at first determined, because nothing would have pointed to the incorrectness of this determination, nothing would have prompted a verification for the difficultly obtained and separated gallium. Here, as in many other instances, a law of nature pointed to the incorrectness which commonly exists in "facts" - which, in essence, are data as "fabricated" ("sdelannye") as the laws of nature themselves.[134]

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[132] Comptes Rendus, 82 (1876) 1036-1039.

[133] Ibid., 83 (1876) 611-3.

[134] The periodic lawfulness of the chemical elements (R.), 1898, p.319, footnote (PLBA, 262).

2. Other predictions made by Mendeleev concerning the existence and properties of unknown elements

The predictions considered in this section will be discussed in various sub-sections distinguished according to the particular region of the periodic system to which a given predicted element was claimed to belong. This form of presentation is more convenient, and probably more natural, than one ordered solely chronologically, since the same or related predictions are often found to recur at different stages of Mendeleev's career.

a) "Pre-hydrogen" elements; the question of the lower limit of the periodic system

In his Attempt at a chemical conception of the world-ether (R.), published in 1903 and 1905,[135] Mendeleev claimed that even as early as 1869 he had entertained the possibility of the existence of chemical elements lighter than hydrogen, and that already in the 1870's it had occurred to him that the luminiferous world-ether might be such an element:

> In 1869, when ... I showed the periodic dependence between the properties of all elements and their ... atomic weights, ... the system of elements began with group I and with series 1, where hydrogen, the lightest of the elements, was placed (and is still placed) ... Never did it enter my head that hydrogen must actually be the first in the series of elements, although there was not at the time, and there still is not, a single other known elementary or compound body lighter than it.[136]

> ... in 1869, when the periodic system was set up, ... it crossed my mind that we could expect some elements preceding hydrogen, with atomic weights smaller than 1, but I did not dare to put forward such a suggestion because it was purely conjectural, and especially because I was afraid of damaging the impression made by the newly-proposed [periodic] system by coupling it with this suggestion of elements lighter than hydrogen.[137]

> Already in the 70's the question had firmly entered my head: what is the nature of such an ether [sc. the luminiferous world-ether] in the chemical sense? This question is intimately connected with the periodic system of the elements, and was aroused in me by the latter; but only now have I decided to talk about it.[138]

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[135] See n.80 in Ch.I (p.43). Mendeleev's Attempt at a chemical conception of the world-ether will commonly be referred to simply as Ether in subsequent footnotes in this thesis.

[136] PLBA, 485.

[137] PLBA, 493.

[138] PLBA, 474, footnote.

Although there is no earlier published evidence to support these claims, there does exist an apparently corroborative manuscript note: written near the entry "H=1" at the top left-hand corner of the periodic table 31 (P8) in one of Mendeleev's personal copies of part II of the 1st edition of Principles of Chemistry (R.; 1871) is the query, in Mendeleev's own handwriting, "Is ether the lightest of all?".[139]

On the question of predictions based upon extrapolation of the periodic system, Mendeleev in A natural system of the elements (R.; publ. 1871) pointed to the much greater uncertainty associated with such predictions than with those made by interpolation within the system (examples of the latter being his predictions of the existence and properties of "eka-boron", "eka-aluminium" and "eka-silicon"):

> We have the full right to judge about elements inside the system, within the limits containing many elements which are already known; but we cannot say the same about the elements which should be situated in the extreme parts of the system. Perhaps certain equilibria, i.e. certain atomologues, simply cannot exist, just as certain members of homologous series are not obtained, but under all of the conditions demanded for their formation change into more stable polymers and other forms, as, for example, methylene.[140]

Although Mendeleev went on in this article to cite specific examples of possible extrapolations of the periodic system, extrapolation into the "pre-hydrogen" region was not one of the possibilities which he mentioned.[141] There was at the time no indication afforded by the structure of the periodic system that pre-hydrogen elements might exist.

A concrete basis, in terms of the structure of the periodic system, for an extrapolation of the system into the pre-hydrogen region emerged at around the turn of the 19th century, with the incorporation of the recently-discovered inert gases into the system as a "zero" group (group 0) preceding group I.[142] Since hydrogen in series 1 is placed in group I, the possibility of a vacancy in group 0 in series 1, immediately preceding hydrogen, now became apparent - as was indicated by Mendeleev (by means of a dash) in his

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[139] See Sc.Ar., fotokopiia 29 (following p.218) and p.225.

[140] Op.cit., p.53 (PLBA, 98-9).

[141] The specific examples of possible extrapolations of the periodic table which were mentioned by Mendeleev in this article are considered later in the present chapter, in sub-section C-2-(b).

[142] The placing of the inert gases in the periodic table is considered in Ch.VII, section C.

tables 58 and 64 from the 7th (1902-3) and 8th (1906) editions respectively of Principles of Chemistry. In his Attempt at a chemical conception of the world-ether (1903, 1905) Mendeleev went even further, postulating the existence also of a "zero" series ("series 0") preceding series 1. This new pre-hydrogen series was introduced by Mendeleev in an attempt to incorporate the luminiferous world-ether into the periodic system: the extrapolated place in group 0 immediately preceding H in series 1 was considered unlikely to correspond to an element of such low atomic weight as that required by the ubiquitous ether. Mendeleev postulated the existence of an element "x" (or "newtonium"[143]) occupying the place "0-0" in the zero group and zero series of his extrapolated periodic system, tentatively identifying this lightest element with the ether; in the position "0-1" immediately preceding H he placed an element "y", suggesting that this might be the "coronium" which Young and Harkness had claimed to have discovered (independently) in 1869.[144] In the (short-form) periodic tables which he drew up containing "x" and "y" - i.e. in tables 60, 61 and 62 - Mendeleev separated "y" and Ne into a different sub-group from "x", He, Ar, Kr and Xe, solely, it seems, to preserve the symmetry of the arrangement of the elements occupying the early rows of the table.

The atomic weights of the elements "x" and "y" were estimated by Mendeleev in his Attempt at a chemical conception of the world-ether as: $x \approx 10^{-6}$, $y > 0.4$ (H=1). From a consideration of the atomic-weight ratios,

Group	VII	Cl:F = 1.86
"	VI	S:O = 2.00
"	V	P:N = 2.21
"	IV	Si:C = 2.37
"	III	Al:B = 2.45
"	II	Mg:Be= 2.67
"	I	Na:Li= 3.28
"	0	Ne:He= 4.98,

he concluded that "the ratio in the given series distinctly and progressively

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[143] Ether: PLBA, 499, footnote ("I should like provisionally to call it 'newtonium', in honour of the immortal Newton").

[144] The discovery of "coronium" had been claimed by Young and Harkness on the basis of spectroscopic observations on the solar corona during the solar eclipse of 1869. In 1898 Nasini, Andreoli and Salvadori claimed to have observed a spectrum indicating the present of traces of "coronium" in certain volcanic gases (see Mendeleev's Ether: PLBA, 496).

increases in passing from the higher to the lower groups, changing most between the first and zero groups. It must therefore be supposed that the ratio He:y will be considerably greater than the ratio Li:H, the latter being = 6.97; consequently the ratio He:y will be at least = 10, and probably even greater. Hence ... the atomic weight of y will be not greater than $\frac{4.0}{10}$, i.e. not greater than 0.4, and probably less".[145] As regards the problem of assessing the atomic weight of "x", he at first commented:

> Although it was possible to determine approximately the atomic weight of the element y on the basis of that of helium, the same type of method cannot be used for element x because it stands at the frontier, at the limit, near the zero-point of the atomic weights ... However, noting the ratios of atomic weights Xe:Kr = 1.56:1, Kr:Ar = 2.15:1 and Ar:He = 9.50:1, a parabola of the second order gives us He:x = 23.6:1, i.e. taking He = 4.0, the atomic weight of x = 0.17, which should be considered as the maximum possible value.[146]

Having initially obtained this "maximum possible" atomic-weight value of 0.17 for "x", Mendeleev immediately added, "It is much more likely that the atomic weight of x is very much smaller [sc. than 0.17]".[147] He then went on to estimate the atomic weight of this lightest element on the basis of the kinetic theory of gases, assuming "x" to be the world-ether and recognising that the molecular velocity of such an all-pervading gas must be high enough for it to escape the gravitational attraction of the most massive bodies in the universe:

> The velocity of the molecular motion of a gas ... is calculated by an expression containing a constant ... divided by the square root of the density of the gas (referred to that of hydrogen), and multiplied by the square root of $(1 + \alpha t)$, which expresses the expansion of the gas with temperature ... If our gas has an atomic weight x, and density (referred to hydrogen) of $\frac{x}{2}$,[148] then the velocity of motion of its molecules will be,
>
> $$v = 1{,}843 \sqrt{\frac{2(1 + \alpha t)}{x}} \qquad \text{- (I)}$$
>
> ... As regards the temperature of heavenly space, ... no one has estimated this to be less than -150°, or greater than -40°; normally the limits are taken as -100° and -60° ... We shall, therefore take the mean temperature, $t = -80^{\circ}$; then, with $\alpha = 0.00367$,[149] formula I gives,
>
> $$v = \frac{2{,}191}{\sqrt{x}}, \text{ or, } x = \frac{4{,}800{,}000}{v^2} \qquad \text{- (II).}$$

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[145] Ether: PLBA, 496.

[146] Ether: PLBA, 501.

[147] Ibid.

[148] The gas "x" is assumed to be monoatomic like the inert gases.

[149] Mendeleev here appends the following footnote (PLBA, 504): "According to the researches of Mendeleev and Kaiander, hydrogen at low and high pressures (up to 8 atmospheres) maintains a coefficient of expansion of about 0.00367, but gases with greater molecular weight give greater values. For lighter gases such as x, we can take no other value but that found for hydrogen."

... The velocity must now be determined ... For our purposes, i.e. for determining the minimum velocity required for a gas molecule to be able to escape into space from the gravitational field of a heavenly body, we need consider only stars of much greater mass than the sun. The double star γ Virginis ... has a common mass about 33 times that of the sun. There is no reason for thinking that this is the maximum, and it will therefore be safer to assume that there may be stars whose mass is 50 times that of the sun; but masses much larger than this I do not consider likely ... For the purposes of our calculation the average density of the large stars may be assumed to be about the same as that of the sun, and therefore ... the radius of a star whose mass is n times that of the sum will be $3\sqrt{n}$ times the radius of the sun ... The velocity required by bodies to escape from the surface of a star 50 times more massive than the sun ... will be about $\sqrt{\frac{2 \times 65 \times 10^{20}}{26 \times 10^{6}}}$ or 2,240,000 metres per second.

... Therefore, it seems to me that the velocity of the molecules of our gas must, in order to permeate space, be greater than 2,240,000 metres per second, and probably less than 300,000,000 metres per second.[150]

Hence, the atomic weight of x, the lightest elementary gas, permeating space and performing the role of the world-ether, must (from formula II) be between 0.00000096 and 0.000000000053, if H=1. I think it is impossible in the present state of knowledge to admit the latter value, because this would in some measure correspond to a revival of the emission theory of light; I consider that for the understanding of the majority of phenomena it is quite adequate to assume that the molecules and atoms of the lightest element x, capable of moving freely everywhere in the universe, have a weight approximately one millionth that of the hydrogen atom, and move with a mean velocity of about 2,250 kilometres per second.[151]

In table 62, accompanying the 2nd edition (1905) of his Attempt at a chemical conception of the world-ether (R.), Mendeleev appears to acknowledge the possibility of the existence in series 0 not only of the element "x" (in group 0) but also of unknown elements in groups I - VII of this series: dashes have been inserted in the places I - 0, II - 0, ... VII - 0 in table 62, in just the same way as missing elements are indicated elsewhere in the table.[152] The possibility of the existence of elements other than merely "x" in series 0 is presumably what Mendeleev had in mind when he wrote in a footnote in his Attempt at a chemical conception of the world-ether:

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[150] 300,000,000 metres per second is the speed of light.

[151] Ether: PLBA, 501-11.

[152] In the corresponding table from the 1st edition of Ether (1903), table 60, there are no dashes in the places I - 0, II - 0, ... VII - 0; nor are there any such dashes in table 61 (1904).

> It seems to me conceivable that the world-ether is not a completely uniform gas, but a mixture of a few gases close to the minimum (predel'nomu), i.e. composed, like our earth's atmosphere, of a mixture of a few gases. But if we were to assume this we would complicate even more the consideration of the subject, and therefore for the sake of simplicity I shall talk only of a uniform limiting (predel'nom) gas which is able to show the properties belonging to the ether.[153]

Among the various factors which led Mendeleev to the publication in the early 20th century of his particular conjectures concerning the existence and properties of elements with atomic weights smaller than that of hydrogen, we can distinguish three types: first, those factors which encouraged him in his "chemical conception" of the ether; secondly, factors which provided him with grounds for an extrapolation of the periodic system into the pre-hydrogen region but which had no direct bearing upon the question of the nature of the ether; and thirdly, certain factors which merely helped to encourage him actually to publish what he himself acknowledged as being no more than extremely tentative ideas. The factors of the first kind, which directly encouraged Mendeleev towards a "chemical conception" of the luminiferous world-ether, were as follows:-

i) Mendeleev was guided in his attempt to provide a "chemical conception" of the ether by a belief in the unity of the sciences. He felt that a true conception of the ether must provide an indication of the chemical significance of this substance, of its relationship to other substances, and therefore of the nature of its subjection to the periodic law; and since the ether must obviously be much lighter than hydrogen, an extrapolation of the periodic system into the pre-hydrogen region is required to satisfy this demand. The influence in this respect of Mendeleev's belief in the unity of the sciences is clearly seen from the following passages written by him in 1902:

> In endeavouring to attach to the conception of "ether" a chemical, and therefore real, possibility, in harmony with the purely real periodic law, I consider that I am doing my best to serve the cause of the unity of science ...[154]

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[153] Ether (2nd edn., 1905): PLBA, 484, footnote. Ether (1st edn., 1903) has "conciseness" (kratkosti) rather than "simplicity" (uproshcheniia), and "which is able to play the role of the ether" rather than "which is able to show the properties belonging to the ether".

[154] Pr.Ch., R-7 (1902-3): Colls., 24, 43, n.6.

> ... all the present-day fundamental conceptions of science - and consequently the conception of the ether - must necessarily be considered under the combined influence of mechanical, physical and chemical knowledge; and ... the thoughtful investigator, seeking true reality, ... is forced to ask himself the question: what is the chemical significance of this substance [sc. the ether]?[155]

> A real conception of the ether cannot be attained if we ignore the question of its chemism, and do not recognise it as an elementary substance; and these days no elementary substance is conceivable which is not subject to the periodic law.[156]

ii) Spectroscopic observations which had been made on such phenomena as the solar corona and the aurora borealis, and also the observed tendency of helium to pass through various solid barriers, suggested to Mendeleev that the inert gases represent "a kind of transition" to the substance of the ether:

> Because the spectral lines of helium are observed for the sun and for certain stars, and those of krypton and the others [sc. the other inert gases] have been seen in the solar corona, the zodiacal light and the aurora borealis, we may suppose that these gases enter into the composition of interplanetary space, and are connected with the substance which forms the "ether".[157]

> ... helium, argon and the other [inert] gases ... evidently present a kind of transition to the substance which fills heavenly space, as is seen from investigations of the solar corona, aurora borealis, etc.[158]

> ... helium at 200° and especially at higher temperatures is able to pass through porcelain, glass, platinum and fused quartz, which, in my opinion, is as though helium and the argon gases in general constitute a transition to the all-pervading universal (luminiferous) ether.[159]

iii) Before the discovery of the inert gases in the 1890's there were no solid grounds for assuming the existence of chemical elements which lacked the faculty for chemical combination, as the ether would have to. But with the discovery of the inert gases a real basis was provided for assuming the ether to be a completely inert chemical element. Mendeleev expressed this point in his Attempt at a chemical conception of the world-ether:

> A few years ago it would have been completely arbitrary ... to deny the existence in the substance or atoms of ether of any faculty for forming compounds with other chemical elements, because until

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[155] Ether: PLBA, 477.

[156] Ether: PLBA, 500.

[157] Pr.Ch., R-7 (1902-3); R-8 (1906), n.167 (PLBA, 522).

[158] Pr.Ch., R-8 (1906) n.565, p.735 (PLBA, 527).

[159] Pr.Ch., R-8 (1906) n.165.

> fairly recently all known elements ... entered, directly or indirectly, into mutual combinations ... But then, in 1894, Lord Rayleigh and Professor Ramsay discovered argon ..., and found it to be the most inactive of all known substances. This was soon followed by the discovery of helium ..., and subsequently ... neon, krypton and xenon. None of these five gases has yet given any definite compounds ... We therefore now have every right to say that the ether is unable to form any stable compounds with other chemical atoms, although it permeates all substances.[160]

iv) The nature and properties of radioactive substances suggested to Mendeleev that radioactivity is probably connected with the ability of a substance to absorb and emit ether from and into the surrounding space, a feeling which encouraged him in his interpretation of the ether as the lightest chemical element, "x":[161]

> It seems to me that radioactivity is probably connected with the power of a substance to absorb from, and emit into, the surrounding space some peculiar unknown substance, allied perhaps to that which forms the world-ether and permeates all bodies. Two circumstances seem especially to indicate that this is so: in the first place helium, argon and the other [inert] gases are found in a peculiar (occluded or combined?) state in uranium and throium minerals, and these gases evidently present a kind of transition to the substance which fills heavenly space ...; and in the second place the Curies and others, by heating native uranium compounds, have obtained a gas which at first possesses radioactive properties but then loses these properties.[162]

v) Another phenomenon which helped lead Mendeleev to his idea of the ether as element "x" was that of the increased phosphorescence of certain substances at very low temperatures:

> I shall briefly mention another phenomenon which has led me to that conception of the ether which I have presented. Dewar, in about 1894, ... noticed that the phosphorescence ... of many substances, especially of paraffin, becomes much more intense at the temperature of liquid air ... It appears to me now that this is due to the fact that paraffin and substances like it have a great capacity for condensing the atoms of ether at very low temperatures, or, more simply, that the solubility (absorption) of the ether increases ... These substances therefore phosphoresce more strongly, because vibrations of light are then set up in the phosphorescent substances not only by their own atoms - which have the property, as a result of illumination at their surface, of passing into a state of peculiar tension which causes the ether to vibrate when the act of illumination ceases - but also by the atoms of the ether which condense in these bodies and set up a state of rapid interchange with the surrounding medium.[163]

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[160] PLBA, 481-2.

[161] Mendeleev's qualitative explanation of radioactivity in terms of the absorption and emission of "x" is presented in Ch.I, pp.44-5.

[162] Pr.Ch., R-8 (1906) n.565, p.735 (PLBA, 526-7).

[163] Ether: PLBA, 515-6.

Factors which provided Mendeleev with grounds for extrapolation of the periodic system into the pre-hydrogen region while having no direct bearing upon the question of the nature of the ether were:-

i) Mendeleev was stimulated in his extrapolation of the periodic system into the pre-hydrogen region by a desire to complete the system, to establish the lower limit of the system:

> Of course this [sc. conception of the ether as the lightest chemical element] is an hypothesis, but one which is stimulated not by purely "working" requirements, but directly by a definite yearning to complete the real periodic system of the known chemical elements at the limit or boundary of the lowest dimension of atoms ...[164]

ii) Mendeleev recognised the placing of the inert gases in group 0, preceding group I, as introducing into the periodic system a definite basis for extrapolation into the pre-hydrogen region. He saw this placing of the inert gases not only as indicating the likelihood of the existence of a lighter inert gas ("y") immediately preceding hydrogen in series 1, but also as providing grounds for introducing in addition a "zero" series, the reasoning in the latter case appearing to be that the demonstration of the existence of a group (viz. the inert-gas group) preceding the hydrogen group in the periodic system provides grounds for expecting the corresponding existence of a series preceding the hydrogen series:

> At the present time, when there remains not the slightest doubt that group I, which contains hydrogen, is preceded by a zero group containing elements of lesser atomic weights than the elements of group I, it seems to me impossible to deny the existence of elements lighter than hydrogen.[165]

> As a consequence of this [sc. satisfactory placing of the inert gases in a zero group preceding group I] ... we can ... expect elements of a zero series with atomic weights much smaller than that of hydrogen.[166]

iii) The solar "coronium" claimed to have been discovered by Young and Harkness appeared to be lighter than hydrogen: "Because an element possessing an independent spectrum has been observed in the solar corona at an altitude above the region of luminous hydrogen, this element, which has therefore been named 'coronium', ... should be characterised by a density, and therefore also an atomic weight, lower than that of hydrogen".[167] Mendeleev felt that

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[164] Ether: PLBA, 499-500.

[165] Ether: PLBA, 493.

[166] Pr.Ch., R-8 (1906) 613 (PLBA, 316).

[167] Elements (chemical) (R.), Bibl.11, vol. 40, half-vol. 80, 1904, p.635 (PLBA, 421).

the inclusion of "coronium" (identified with element "y") in group 0 of the periodic table was supported by the fact that helium also had originally been characterised solely on the evidence of the solar spectrum, and by the fact that the spectrum of coronium "is simple, just as the spectrum of helium is simple".[168]

Finally, there were certain factors which served merely to encourage Mendeleev actually to publish his conjectures on the "chemical conception" of the ether:-

i) By 1902, when Mendeleev wrote his Attempt at a chemical conception of the world-ether, the periodic law was well-established, and was no longer likely to be unjustly discarded by the scientific community merely because of false or unfulfilled predictions concerning its possible extension.[169]

ii) By the early 20th century Mendeleev had come to believe that the solution to the mysteries of modern science lay in the determination of the true nature of mass and the ether, and not in such ideas as postulated a single primary matter, complexity of the elements, and the decomposition of chemical atoms.[170] No-one, however, had attempted to provide an alternative explanation in terms of the ether for phenomena (such as those associated with radioactivity) which many had begun to explain in terms of the dissociation of atoms. Publication of such an alternative approach was therefore considered by Mendeleev to be urgently required, if only to stimulate other, improved, contributions to the field. In his Attempt at a chemical conception of the world-ether Mendeleev wrote:

> ... in recent years there has frequently been much talk about the division of atoms into more minute electrons, and it seems to me that such an idea should be considered not so much metaphysical as metachemical, proceeding from the absence of any definite notions regarding the chemism of the ether, and it is my desire to replace such vague ideas by the more real notion of the chemical nature of the ether. For until someone demonstrates either the transmutation of ordinary matter into ether, or vice versa, or else the transmutation of one element into another, any idea of the dissociation of atoms must, in my opinion, be considered contrary to the teachings of modern science; and those phenomena in which a division of atoms is claimed may be understood as an emission of the generally-acknowledged all-permeating ether. In short, it seems to me that the time has come

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[168] Ether: PLBA, 496.

[169] See Mendeleev's comments in Ether, PLBA, 485-6, 493.

[170] See Mendeleev's comments of the early 20th century quoted in Ch.I, p.43, and Ch.V, p.306.

> to speak, even if only speculatively, about the chemical nature of the ether, especially as no-one to my knowledge has yet spoken at all definitely on this subject ...; perhaps my imperfect thoughts will lead someone to a surer path than that which could possibly be shown to my enfeebled vision.[171]

iii) By 1902 Mendeleev was an old man who realised he had little time left to live, and he did not want his thoughts on the nature of the ether to be utterly wasted:

> ... I would readily still remain silent, but I now have no years ahead of me ...[172]
>
> ... because of my old age I think that I cannot delay.[173]
>
> I do not want these thoughts, which have been suggested by facts, to be wasted.[174]

b) Elements between H and Ca.

The earliest predictions by Mendeleev of unknown elements with atomic weights falling between H=1 and Ca=40 appear to have been those given in two manuscripts of March 1869, tables 3 (M3) and 7 (M7). In the horizontal long-form periodic table 3 (M3) two unknown elements of atomic weights 8 and 22 are included as lower analogues of Cu, giving the series: H = 1, ? = 8, ? = 22, Cu = 63.4, Ag = 108, Hg = 200. These two elements "? = 8" and "? = 22" cannot be regarded as representing Li and Na, because the latter elements are included elsewhere in table 3 (M3), as Li = 7 and Na = 23. Table 7 (M7) was not a periodic table, but a table of elements arranged in two columns according to whether they show even or odd valency, the elements within each column being ordered according to atomic-weight value: the first entry in the even-valent column, "H^2 = 2", is quite possibly intended to represent an unknown even-valent element of atomic weight 2, rather than merely the hydrogen molecule; and appended to the table are two queries, suggesting, on the basis of the atomic-weight differences in the even-valent column, that even-valent elements "x = 20" and "x = 36" might perhaps exist.[175] These early manuscript predictions never appeared in published form: table 7 (M7) was not published at all; and although table 3 (M3) was the manuscript upon which the published forms of Mendeleev's "attempt at a system",

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[171] PLBA, 486-7.

[172] Ether: PLBA, 474, footnote.

[173] Ether: PLBA, 486.

[174] Ether: PLBA, 516.

[175] The entries "H^2 = 2", "x = 20" and "x = 36" in table 7 (M7) have been considered by Kedrov to represent an anticipation by Mendeleev of the existence of He, Ne and Ar (see Ch.VII, section C).

tables 8 (P1) and 9 (P2), were based, the entries "? = 8" and "? = 22" were removed from the table by Mendeleev at the proof stage of the first published version, table 8 (P1), leaving two unmarked empty places between H and Cu.

In his discussion of his "attempt at a system", table 9 (P2), in Correlation of properties (R; 1869), Mendeleev made the following general remarks about the occurrence and significance of gaps in the table:

> The first column is for elements with small atomic weights, like Li and H, and there are thus 6 columns ... into which all the elements are distributed in a few horizontal rows, the members of which show chemical resemblance. Only the one row of Li and Na has representatives in all columns: the other rows have representatives in only certain of the columns, so that free places are created for elements which may perhaps be discovered in due course.[176]

To the concluding comment of this passage Mendeleev appended the footnote, "We could perhaps place Li above Be, and Mg below Na". A little later in the same article, however, he claimed:

> ... there seems to be no doubt, looking at the accompanying table [sc. table 9 (P2)], that ... in the calcium row the members analogous to Na and Li are missing; Mg to some extent corresponds to the analogue of Na, but Mg cannot be placed in the row of Ca, Sr and Ba, as is shown not only by the properties of certain compounds of these elements, but also by the physical properties of the metals themselves, and, to a certain extent, of their compounds.[177]

This prediction of the existence of two missing lower analogues of Ca, as also the prediction of the elements "? = 8" and "? = 22" in table 3 (M3) and the corresponding tacit suggestion of two missing elements between H and Cu in tables 8 (P1) and 9 (P2), turned out to be false, having arisen from the defective arrangement of certain elements in Mendeleev's original "attempt at a system". The arrangement of elements in the (short-form) table 10 (P3), which was published at the same time as table 9 (P2) in Correlation of properties, already neither suggested the existence of unknown lower analogues of Ca nor contained empty places corresponding to those found between H and Cu in table 9 (P2).

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[176] Op.cit., pp. 72-3 (PLBA, 27).

[177] Ibid., p.74 (PLBA, 28).

In his Correlation of properties Mendeleev expressed the view that it would be "especially desirable to add to the number of elements standing closest to hydrogen [sc. in table 9 (P2)]. These elements, which would represent a transition from hydrogen to boron and carbon, would surely constitute the most important of the scientific gains which we might expect from acquaintance with newly discovered simple bodies."[178]

Nearly two years later, in his article A natural system of the elements (R.; publ. 1871), Mendeleev followed his presentation of detailed predictions for those five elements whose existence he considered "extremely probable"[179] - viz. the elements "eka-boron", "eka-aluminium", "eka-silicon", "dvi-boron" and an element occupying position III-6 in table 30 (P7) - with a discussion of the possibility of the existence of various other unknown elements "whose very existence is to some extent still subject to doubt".[180] He wrote here, "perhaps the elements of low atomic weight from 1 to 7, i.e. between H and Li, may be impossible; as also may be elements of group VIII with atomic weights of about 20, i.e. those placed between F and Na, corresponding to the elements of the iron group placed between Mn and Cu."[181]

Mendeleev returned to a consideration of the possibility of the existence of elements between H and Li and in group VIII between F and Na during the second half of the 1890's, in connection with the problem of placing He and Ar in the periodic table.[182] Thus, in 1898, he wrote:

> We may think ... that elements will be discovered in the first series, where at present only hydrogen is known, and also in group VIII between F and Na; but here we have not only the edge of the system, but also the typical elements, and therefore we may expect eccentricity and peculiarity. Perhaps ... helium and argon ... belong to the indicated places ...[183]

In the early 20th century, having now come to adopt the placing of He and Ar in group 0, Mendeleev suggested that the most likely element to exist with an atomic weight between H = 1 and He = 4 would be a new halogen:

> It is perhaps possible that there are also elements with atomic weights greater than H = 1.008 but less than He = 4, from the groups II - VII; ... it seems to me that at present the most likely of all to expect is a halogen, but not elements for all the groups, because in

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[178] Ibid., p.75 (PLBA, 29).

[179] Op.cit., p.44 (PLBA, 89).

[180] Ibid., p.53 (PLBA, 98).

[181] Ibid. (PLBA, 99).

[182] See Ch.VII, section C.

[183] The periodic lawfulness of the chemical elements (R.), Bibl.11, vol.23, half-vol. 45, 1898, p.320 (PLBA, 263). In table 56 (P29), accompanying this article, three vacant places are marked in group VIII between F and Na.

> the first rows we cannot expect representatives of all the chemical functions or groups, just as we do not find them in the last rows, and there are only 4 known halogens, but 5 alkali metals (and members of many other groups)... Perhaps there is a halogen in nature with an atomic weight of about 3.[184]

Mendeleev's belief at this time in the possibility of the existence of elements belonging to groups II - VII in the hydrogen series (i.e. series 1) is to be seen in his inclusion of dashes in the appropriate 6 places in tables 58 (P31), 62 (P35) and 64 (P37), dating from 1903-6.

c) Elements between Ca and Ba

The most detailed and the best known of Mendeleev's predictions concerning unknown elements in the region of the periodic table between Ca and Ba - indeed, the most detailed and the best known of all his predictions - were his strikingly successful predictions of the existence and properties of "eka-boron", "eka-aluminium" and "eka-silicon" (see earlier, pp. 351-68). At the same time as he first presented his detailed predictions for these three unknown elements, in A natural system of the elements (R.; publ. 1871), Mendeleev discussed also the properties of an element which he referred to as "dvi-boron", occupying the place between Sr and Zr in the periodic table.[185] Just as in the case of the elements "eka-boron", "eka-aluminium" and "eka-silicon", Mendeleev was confident of the existence of "dvi-boron"; in fact he acknowledged that this element is "very probably" the known element yttrium,[186] as indeed it turned out to be, although he was not yet prepared unreservedly to identify "dvi-boron" with yttrium because the values which had so far been determined for the equivalent of yttrium corresponded to an atomic weight for trivalent yttrium slightly higher than the accepted atomic weight of 90 for zirconium. By the mid-1870's, by which time Clève had obtained an equivalent of 29.8 for yttrium (giving an atomic weight $3 \times 29.8 = 89$), Mendeleev no longer doubted the placing of yttrium as "dvi-boron" between Sr and Zr.

In A natural system of the elements (1871) Mendeleev had the following to say about "dvi-boron":

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[184] Ether (1903, 1905): PLBA, 493, footnote.

[185] According to Mendeleev's original, incomplete, system of numeration of the series in the short-form periodic table, employed for example in table 30 (P7) in A natural system of the elements (R.; 1871), the place between Sr and Zr is designated III-4. According to the later, complete, system of numeration of the series adopted by Mendeleev before the end of 1871, this same place came to be designated III-6.

[186] Op.cit., p.48 (PLBA, 93).

> The atomic weight of this element should be approximately 89, i.e. mid-way between the atomic weights of Sr and Zr; the atomic volume of the metal should be about 27, and the specific gravity of the metal consequently about 3.3 ... The volume of the oxide ... should be about 45, the specific gravity of the oxide therefore being about 5.0 ... We must think that the oxide of the metal III-4 (if this is not yttrium, then it may be called dvi-boron) of the form R_2O_3 should be an extremely energetic base, because the oxide of zirconium is already a very distinct base ... Comparing the known properties of yttrium with these properties which undoubtedly characterise this metal [sc. the metal III-4, dvi-boron], we may think that yttrium does in fact belong in this place. According to Bunsen's determinations the equivalent of yttrium with respect to hydrogen is 30.8, and therefore, taking R_2O_3 as the formula of yttrium oxide, yttrium should be given an atomic weight of 92, which is extremely close to the atomic weight of the element which should stand in the place III-4.[187]

In table 30 (P7) which accompanied this article the entry in the place III-4 is "(?Yt = 88?)".

Later in 1871, in his article The periodic lawfulness of the chemical elements (G.), Mendeleev wrote:

> ... just as there exists much resemblance between Ca and Sr, and between Ti and Zr, so also will there be many resemblances between eka-boron and dvi-boron (yttrium?). This indicates that the separation of eka-boron from yttrium - if the latter actually is dvi-boron, and if eka-boron accompanies it - will be difficult.[188]
>
> The oxide of dvi-boron - which may be yttria - ... should have a specific gravity of about 4.8.[189]

The tables 35 (P11) and 36 (P12) accompanying this article have "?Yt = 88?" and "?Yt = 88" respectively in the place between Sr and Zr (i.e. in the place which was now designated III-6).

The possibility of the existence of an element belonging between Sr and Zr in the periodic table had already been recognised by Mendeleev as early as 1869. Thus the manuscript tables 5 (M5) and 6 (M6), dating from March 1869, each have a vacant space marked between Sr and Zr, as does the published table 10 (P3) which appeared in the late spring of the same year. Other tables dating from the period prior to the summer of 1870 also have a vacancy indicated between Sr and Zr. In the summer-early autumn of 1870 Mendeleev

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[187] Ibid. The properties which have actually been found for yttrium include the following: atomic weight, 88.2 (H=1); sp.grav. of metal, 4.34 (pykn.), 4.47 (X-ray); atomic vol. (from sp.gr. 4.34), 20.3; formula of oxide, Y_2O_3; oxide is distinctly basic; sp. grav. of oxide, 5.01 (X-ray), giving sp.vol. 44.9.

[188] Op.cit., p.198 (PLBA, 151).

[189] Ibid., p.199, footnote (PLBA, 152).

drew up the manuscript table 16 (M10), in which he placed "Ce La Di 92" between Sr and Zr. Shortly afterwards, in table 17 (M11), he included both "Ce La Di!!" and "Yt 93" in this place. Most of his subsequent manuscript tables of 1870 tentatively include yttrium between Sr and Zr; an exception is table 19 (M13), which lists an estimated atomic volume of 27 for the (unidentified) element assumed to occupy this place.

Somewhat similar to the case of dvi-boron, in the sense of not actually representing the prediction of an unknown element, was Mendeleev's indication in his tables of the period from mid-1869 to mid-1870 of the existence of an element occupying the place between Cd and Sn. Before mid-1869 Mendeleev had included uranium in this place; after mid-1870 he came, correctly, to place indium here. In his tables 12, 13, 14 and 15, however, dating from the intervening period, the space between Cd and Sn was not occupied, but was nevertheless retained by him as undoubtedly corresponding to the place of an element whose identity he had yet to appreciate.

A recognition by Mendeleev of the possibility of the existence of an element occupying the place in the periodic table which turned out to belong to technetium[190] can be traced back as far as his earliest known manuscript short-form table, table 5 (M5), drawn up in March 1869. In a subsequent manuscript periodic table also dating from March 1869, table 6 (M6), there is an indication of an attempt by Mendeleev to estimate an atomic-weight value for such an element: before eventually putting rhodium, as "Ro = 104.4", in the place corresponding to technetium in table 6 (M6), Mendeleev had originally written "? = 103" in this place. The first published attempt by Mendeleev to estimate the atomic weight of a missing element corresponding to technetium appeared in May 1869, in table 10 (P3); but the value given in this table, viz. 190, is clearly a misprint.[191] Mendeleev's next published estimate of the atomic weight of this element did not appear until early 1871, in A natural system of the elements (R.), where he wrote: "... we may expect an element more analogous to manganese than is ruthenium, ..., having a lesser atomic weight than ruthenium, viz. about 100, and belonging to group VII, tending to give a salt KRO_4, like $KMnO_4$".[192] In table 30 (P7), accompanying

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[190] Technetium was discovered in the late 1930's. The only isotope to have been obtained in macroscopic amounts is ^{99}Tc(β^-, 2.12×10^5 years).

[191] In PLBA, p.22, Kedrov has "corrected" this misprint "190" in table 10 (P3) to "106"; however, there seems to be little if any justification for his choice of the particular value 106 rather than, say, 100 (see PLBA, 689).

[192] Op.cit., p.54 (PLBA, 99).

this article, the place corresponding to technetium contains the entry "- = 100". During the second half of 1870 Mendeleev had drawn up a number of manuscript periodic tables containing atomic-weight values for the element in question, the chronological sequence of the values given in these manuscripts being: 98→99→98→100.[193]

In his article The periodic lawfulness of the chemical elements (G.), published in November 1871, Mendeleev introduced the name "eka-manganese" for the missing element corresponding to technetium: he refers to "eka-manganese Em = 100".[194] In this article Mendeleev suggests that if the highest oxide of ruthenium should in fact turn out to have the composition Ru_2O_7 rather than RuO_4, then perhaps the place of "eka-manganese" belongs to Ru, acknowledging that this would of course leave a gap in group VIII.[195] This suggestion represents what seems to have been the last manifestation of a tendency which Mendeleev had shown occasionally since March 1869 to consider placing ruthenium or rhodium in the space belonging to technetium in the periodic table.[196]

In 1881, in a report to a meeting of the chemical section of the Russian Physico-Chemical Society, Mendeleev predicted that "eka-manganese" would have an atomic weight of about 100, that its compounds would be coloured, and that it would form oxides RO, R_2O_3, RO_2, RO_3 and R_2O_7; he now suggested that it might turn out to be a rare-earth element.[197]

Although all of Mendeleev's periodic tables published after 1871 contain a space for a missing element corresponding to technetium ("eka-manganese"), only four of these tables give an estimated atomic-weight value for this element: tables 38 (1873) and 41 (1877) give the value 100, and tables 57 (1902) and 63 (1906) give 99. Appended to each of the last two tables is the

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[193] See the manuscript tables 16, 17, 20, 23, 24, 25 and 26. Table 26 (M19) was the manuscript version of table 30 (P7).

[194] Op.cit., p.205 (PLBA, 157).

[195] Ibid., footnote. In the same footnote Mendeleev suggests similarly that the place of a further expected analogue of manganese, "tri-manganese Tm = 190" (see later), might perhaps belong to Os, adding, "A comparative study of OsO_4 and Mn_2O_7 would be very desirable."

[196] This tendency had been shown in table 6 (M6) (see above); in table 21 (L1), presented in the late autumn of 1870; and in table 27 (L2), presented late 1870-early 1871 but compiled probably in 1869.

[197] J.Russ. Phys.-Chem.Soc., 13 (1881) no. 3, section 1, pp.519-20 (PLBA, 205). Mendeleev seems to suggest that "eka-manganese" might turn out to be a "cerite" or "gadolinite" (i.e. rare-earth) element also in Pr.Ch., R-4, part II (1882) 756. (See Ch.VII, pp. 426 and 427).

footnote, "We may expect the discovery of a metal similar to Mn (eka-manganese) with an atomic weight of ca.99".

In two of Mendeleev's earliest manuscript periodic tables, tables 5 (March 1869) and 11 (spring 1869), not only is a missing element indicated for the place belonging to technetium, but also three further missing elements are indicated for the places actually belonging to Cr, Mn and Mo, these last three elements being erroneously placed instead in that region of the table which later came to be called "group VIII". By mid-1870 Mendeleev appears to have completely rejected this tendency to misplace Cr, Mn and Mo and leave their true places free for missing elements. During the intervening period he sometimes included Cr, Mn and Mo in their rightful places, as in table 15 (P6), and sometimes left these places unoccupied, as in tables 10 (P3), 13 (P4) and 14 (P5); but since the "group-VIII" region is missing from these last three tables it is not clear whether Mendeleev had here for some reason merely omitted Cr, Mn and Mo from their correct places while nevertheless recognising these places as being rightfully theirs, or whether he had considered instead that they should be placed in the (missing) "group-VIII" region.

A further prediction of the possible existence of missing elements belonging to the region of the periodic table between Ca and Ba was made by Mendeleev in the following passage from A natural system of the elements (R.; 1871):

> Perhaps also there exist elements analogous to Na in group I, having atomic weights close to those of Cu and Ag, although these latter metals also tend, like Na, to form compounds RHO, RCl, etc., and therefore perhaps constitute a transition from the elements of group VIII to the elements of group II.[198]

This suggestion of the possible existence of two missing analogues of Na in group I was not made elsewhere by Mendeleev. It is not even reflected in table 30 (P7), the periodic table accompanying the article A natural system of the elements: in table 30 (P7), as in all of the subsequent short-form periodic tables published by Mendeleev, Cu and Ag (and also Au) are included both in group I as analogues of Na and in group VIII (see Ch.V, n.69).

d) Elements between Ba and Ta.

We can recognise four stages of development in Mendeleev's opinion concerning the total number of elements likely to exist with atomic weights falling between those of Ba (ca.137) and Ta (ca.182). The brief initial stage was that shown in his original horizontal long-form periodic classification

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[198] Op.cit., p.54 (PLBA, 99).

of the elements which was drawn up in March 1869 - his "attempt at a system", tables 3 (M3), 8 (P1) and 9 (P2). The only element indicated between Ba and Ta in this "attempt at a system" was an unknown element marked as "? = 180": this element "? = 180" may be seen as corresponding to the element hafnium (Hf = 177.1, taking H = 1; discovered in 1923), not just according to the value of its atomic weight but also because in the "attempt at a system" it occupies the place immediately preceding Ta and represents a higher analogue of Ti and Zr. The second stage in the development of Mendeleev's opinion regarding the number of elements existing between Ba and Ta in the periodic table emerged with his transition, already evident in manuscripts of March 1869, from the original long-form "attempt at a system" to a short-form arrangement of the elements, and lasted until the summer-early autumn of 1870. During this period Mendeleev appears to have felt that there are 9 elements possessing atomic weights between those of Ba and Ta, Ba and Ta being placed at this time in consecutive series in the short-form classification; towards the very end of the period he attempted to place Ce (with an atomic-weight value of 138) and Th (with an atomic-weight value of 174) in this region of the table, but prior to this he had not suggested that any of the assumed 9 elements between Ba and Ta might already be known. The third stage which can be distinguished in Mendeleev's view of the likely number of elements between Ba and Ta lasted from the summer-early autumn of 1870 right up to the end of the 19th century. Mendeleev now classified Ta not in the series in the short-form table immediately following that containing Ba, but in the next series again, so that a completely unoccupied series separated the Cs-Ba series from the Ta-W series, giving altogether 19 places for elements between Ba and Ta. In his tables of this period Mendeleev consistently attempted to place a few of the known lanthamide elements in some of the places between Ba and Ta (this is discussed in detail in Ch.VII, section B). The fourth and final stage in Mendeleev's opinion concerning the number of elements between Ba and Ta in the periodic table lasted from 1900 to the end of his life, and was merely that modification of stage 3 which resulted from the incorporation into the periodic table of the "zero" group of inert gases: with this extension of the number of groups there were now 20 places for elements between Ba and Ta in Mendeleev's periodic table, not 19 as in stage 3.

The available evidence relating to the second stage of development of Mendeleev's opinion regarding the number of elements with atomic weights between those of Ba and Ta appears to be confined solely to seven of the tables drawn up by him during the period from March 1869 to the summer-early autumn 1870, viz. tables 5 (M5), 6 (M6), 10 (P3), 11 (M8), 15 (P6), 16 (M10) and 17 (M11). All of these tables except table 15 (P6) have 9 places for the elements between Ba and Ta, as indicated below in Fig. VI-1 (where the

Table 5 (M5)	Cs = 133	Ba = 137	?		?	?	?
	?	?	?	?	Ta = 182	[etc.]	
Table 6 (M6)	Cs = 133	Ba = 137	—	—	—	—	? = 157
	? = 165	? = 170	? = 175	? = 180	Ta = 182	[etc.]	
Table 10 (P3)	Cs 133	Ba	—	—	—	—	160
	—	—	—	—	Ta	[etc.]	
Table 11 (M8)	Cs = 133	Ba = 137	—	—	—	—	—
	—	—	—	—	Ta = 182	[etc.]	
Table 16 (M10)	Cs = 133	Ba = 137	Ce 138				
			?! Th = 174		Ta = 182	[etc.]	
Table 17 (M11)	Cs = 133	Ba	Ce = 138	? Ce = 138		? 143	? 145
					Ta 182	[etc.]	

Fig. VI-1.

appropriate reproduced regions of the tables have been standardised to the vertical form of arrangement for convenience of comparison). Table 15 (P6), on the other hand, contains only 2 places for elements between Ba and Ta. This unique feature of table 15 (P6) is nowhere commented upon by Mendeleev. It is extremely unlikely that table 15 (P6) actually reflects a belief by Mendeleev that there might exist only two elements with atomic weights between 137 and 182, since this would entail anomalously large atomic-weight differences for adjacent elements in this region of the table (it seems to have been a consideration of atomic-weight increments in the periodic table which had already prompted Mendeleev's introduction of 9 places between Ba and Ta in March 1869,[199] and which in the summer-early autumn of 1870 led him to increase this to 19 places[200]). That Mendeleev might have been entertaining the idea that more than one element occupies one or both of the places between Ba and Ta in table 15 (P6), thus perhaps anticipating to some extent the present-day mode of classification of the lanthanide elements, is equally unlikely, since except for the special case of group VIII he was always strongly committed to the assumption of single-occupancy of places in the periodic table. If the arrangement of elements in the final row of table 15 (P6) is not simply a printing error, then it seems the most likely that in this table Mendeleev had telescoped the region between Ba and Ta either for reasons merely of compactness of presentation rather than for any theoretical reasons, or else possibly on the basis of symmetry considerations concerning the relative placing of the iron, palladium and platinum families, but if so without thought for the implications of this symmetry-based judgment for the region between Ba and Ta.

The predictions presented by Mendeleev in tables 5 (M5), 6 (M6), 10 (P3), 11 (M8), 16 (M10) and 17 (M11) concerning the region of the periodic system between Ba and Ta (see Fig. VI-1) were, quite understandably, based upon his assuming for this region the pattern of periodicity which had been shown by the elements lighter than Ba, and which was already becoming apparent to some extent also for the known elements heavier than Ta. However, the pattern of periodicity shown by the elements preceding Ba and immediately following Ta in fact breaks down in the region between Ba and Ta, where it turns out that there are actually 16 elements, of which 14 (viz. the lanthanide elements Ce - Lu) require what is effectively an extension of the periodic table into a third dimension for them to be satisfactorily classified. We must therefore

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[199] Mendeleev's concern with atomic-weight differences in March 1869 is clearly seen in table 6 (M6)(a).

[200] See later.

regard Mendeleev's "second-stage" predictions for the region between Ba and Ta (Fig. VI-1) to be false - at least, predominantly so.[201] Both of the two subsequent stages which we have recognised in Mendeleev's opinion regarding the number of elements between Ba and Ta were similarly based upon an erroneous extension into this region of the table of the pattern of periodicity established for the lighter and (to a lesser extent) heavier elements.[202]

Mendeleev's introduction into the periodic table in the summer-early autumn of 1870 of what in the short-form arrangement consisted of new, completely unoccupied, series between the Cs - Ba series and Ta - W series seems to have been prompted by a consideration of the atomic-weight differences in a table which now classified Hg, Tl, Pb and Bi in their correct groups.[203] In a manuscript note accompanying the long-form table 18 (M12), dating from the summer-early autumn of 1870, Mendeleev wrote, "A break in continuity is most noticeable in going from Ba = 137 to Ta = 182, since the atomic-weight interval Ca - Ti = 10, [Sr - Zr = 9] but Ba - Ta = 45".[204] For a horizontal long-form table like table 18 (M12)

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[201] We could perhaps claim that despite the false basis of Mendeleev's prediction of elements between Ba and Ta in the 6 tables represented in Fig. VI-1, the elements "? = 175" and "? = 180" given in table 6 (M6) may to some extent nevertheless be considered to correspond respectively to lutetium and hafnium. Thus Lu = 173.5 (H = 1) has an atomic weight close to 175, it is indeed the second element before Ta in the periodic table (in terms of atomic number), and it is considered to belong to group III; Hf = 177.1 (H = 1) has an atomic weight fairly close to 180, it immediately precedes Ta in the periodic table, and it belongs to group IV.

[202] However, the possibility of a "break in the form" of the periodic system in the region between Ba and Ta was in fact acknowledged by Mendeleev, notably in 1870-1 and in the early 20th century (see later in the present chapter, and also Ch.VII, section B).

[203] It seems to have been his erroneous placing of the elements Hg, Tl, Pb and Bi - especially that of Pb - which had discouraged Mendeleev from introducing a new, unoccupied, series between the Cs - Ba series and Ta - W series in the short-form table 6 (M6), March 1869 (see Ch.III, p.183). With the correct placing of Hg, Tl, Pb and Bi this extra series could not be introduced into the periodic table. In fact Hg, Tl, Pb and Bi had come to be correctly placed as early as the summer of 1869, in table 12 (M9), but Mendeleev seems not to have considered the question of the atomic-weight difference between Ba and Ta in the light of this new arrangement of Pb, etc., until the summer-early autumn of 1870.

[204] See Sc.Ar., 103.

the most obvious and satisfactory solution to the problem of the anomalously large unoccupied atomic-weight region between Ba = 137 and Ta = 182 would seem to have been the introduction of a complete new column of places for elements between the Zr - Ba column and Ta - Bi column. This was not actually done in table 18 (M12); but very shortly afterwards Mendeleev introduced a corresponding extension in the short-form manuscript table 19 (M13), the earliest known table to reflect what we have recognised as the third stage in Mendeleev's opinion regarding the number of elements between Ba and Ta. Table 19 (M13) and the table 20 (M14) which was drawn up soon after do not yet show whether Mendeleev intended to include places for a new family of 3 elements in the Cs - Ba series analogous to the iron, palladium and platinum families - i.e., from tables 19 (M13) and 20 (M14) it is not clear whether Mendeleev now considered the number of elements between Ba and Ta to be 16 or 19. By the late autumn of 1870, however, Mendeleev had begun to draw up manuscript tables containing a clear indication that he was indeed introducing three new places between those of the palladium and platinum families in what by now he had come to call "group VIII", giving altogether 19 places between Ba and Ta in the periodic table (see, for example, table 23).

The predictions given by Mendeleev for the region between Ba and Ta in table 19 (M13) and six subsequent tables dating from the period up to the end of 1870 are indicated below in Fig. VI - 2 (standardised to the vertical short-form arrangement). The atomic weights 163 and 191 given in table 24 (M17) for the elements which we could refer to (using Mendeleev's system of nomenclature) as "eka-cadmium" and "eka-barium" respectively seem to have been estimated by Mendeleev solely on the basis of a consideration of diagonal atomic-weight trends in the table[205]; there are no grounds for thinking that the value 191 for the atomic weight of "eka-barium" was entertained as a serious possibility by Mendeleev when he saw that it violated the principle of atomic-weight ordering (see n.1 to the present chapter). The last two periodic tables represented in Fig. VI - 2, viz. tables 25 (M18) and 26 (M19), were the manuscript final drafts of the published tables 33 (P10) and 30 (P7) respectively. Table 33 (P10) appeared in the article On the place of cerium (G.; March 1871), and table 30 (P7) in A natural system of the elements (R.; Feb. 1871), these two articles, together with the tables 31 (P8) and

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[205] See table 24 (M17) (a), and Fig. V - 4. The terms "eka-cadmium" and "eka-barium" were not actually used by Mendeleev himself in connection with table 24 (M17); he did much later (during the period from 1889 onwards) talk of "eka-cadmium", but seems never to have used the term "eka-barium".

	I	II	III	IV	V	VI	VII	VIII
Table 19(M13) [Atomic vols.]	Cs=60	Ba=38	La=30	Ce=25				
	—							
	—				Ta	[etc.]		
Table 20(M14)	Cs=133	Ba=133	?=135 / La	?138 / Ce	?Di=143?	—	—	
	—	—	?Er=?168·9?	—			—	
	—	—	—	?=180	Ta=182	[etc.]		
Table 21(L1)	Cs=133	Ba=137	—	—	—	—	—	Ce=?
	—	—	—	—	—	—	—	
	—	—	—	—	Ta=182	[etc.]		
Table 23(M16)	Cs=133	Ba=137	La	Ce=138	—	—	—	— — —
	—	—	—	—	—	—	—	
	—	—	Er	Di	Ta=182	[etc.]		
Table 24(M17)	Cs=133	Ba=137	[Di=139?] La	Ce=138?	~~[Di=140?]~~	—	—	[Ce? La? Di? Er?]
	—	163	—	—	—	—	—	
	—	191	—	—	Ta=182	[etc.]		
Table 25(M18)	Cs=133	Ba=137	[Di=143?]	Ce=138	—	—	—	[La? Di? Er?] —
	—	—	—	—	—	—	—	
	—	—	—	—	Ta=182	[etc.]		
Table 26(M19)	Cs=133	Ba=137	—=137	Ce=138?	—	—	—	———
	—	—	—	—	—	—	—	
	—	—	—	—	Ta=182	[etc.]		

Fig. VI-2.

32 (P9) in Part II of the 1st edition of Principles of Chemistry (R.; Feb. 1871), providing the earliest published indication of the third stage in Mendeleev's opinion regarding the number of elements occupying the region of the periodic table between Ba and Ta.

In On the place of cerium Mendeleev presented his reasons for placing Ce in the position IV - 6 in table 33 (P10),[206] and on the subject of elements coming between Ce and Ta in the table he wrote, "... at present not a single element is known for certain from the two series beginning with V - 6 and ending with IV - 8".[207] The place III - 6 in table 33 (P10), as in table 25 (M18), contains the entry "(Di = 143?)". Among the predictions which he made in his article A natural system of the elements concerning elements whose existence he considered "extremely probable", Mendeleev included not only those for "eka-boron", "eka-aluminium", "eka-silicon" and "dvi-boron", but also certain predictions for an element occupying the position III - 6 in table 30 (P7), between Ba and Ce:

> In the same way [sc. as for "dvi-boron", in the place III - 4] we can deduce the properties of the element standing in the place III - 6, which must have an atomic weight of about 137. This element should form an energetic oxide of composition R_2O_3. In the free state it should have a volume of approximately 30, and consequently a specific gravity close to 4.5; its oxide should have a volume of ca. 52, and consequently a specific gravity of ca. 6.2. These properties are close to those of lanthanum and didymium ... But whether one of those two metals does in fact belong in the place indicated, and if so which one, can be shown only by further, more detailed, investigations of didymium and lanthanum in their compounds.[208]

Later in the same article Mendeleev discussed the question of the occupancy of the region of table 30 (P7) between Ce (placed in IV - 6 as "Ce = 138?") and Ta (V - 8, "Ta = 182"):

> I draw attention ... to the striking fact that the system of the elements at present lacks exactly 17 elements (i.e. an entire two-series period) having atomic weights between 138 and 182. This phenomenon is hardly fortuitous (sluchaino), because both in the region of smaller atomic weight and in the region of greater atomic weight extremely many elements are known to us. It may be, however, that certain cerite metals will be placed in this space, because by ascribing the composition R_2O_3

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[206] See sub-section B-1-(c) of the present chapter.

[207] Op.cit., p.51 (PLBA, 66).

[208] Op.cit., pp. 48-9 (PLBA, 93-4). The placing of La and Di in the periodic table by Mendeleev is discussed in Ch.VII, section B.

or RO_2 to their usual oxides we obtain atomic weights for them from 140 to 180, if the determinations of their equivalents known at present be sufficiently precise.[209]

The probable meaning of the comment in this passage that "this phenomenon is hardly fortuitous" is indicated to some extent in a similar remark published fairly soon afterwards by Mendeleev in his article The periodic lawfulness of the chemical elements (G.; Nov. 1871), and to a greater extent in the more explicit original Russian manuscript draft of this latter remark (see below, p.396). What Mendeleev appears to have meant is that it is hardly because of sheer bad luck that the elements which would be expected to exist with atomic weights between those of Ce and Ta had not been discovered, but is perhaps instead because there is some unknown factor in the very nature of the chemical elements which has resulted in the instability or non-existence of the elements expected for this region of the periodic table.

In a manuscript note dating apparently from late 1870 or early 1871 we find the only known instance of Mendeleev's use of the term "eka-molybdenum"; in this note Mendeleev assigns "eka-molybdenum" an atomic weight of 140, and appears to be suggesting that because "eka-aluminium" and "eka-molybdenum" should both have equivalents close to that of zirconium, they might perhaps be found to occur naturally in admixture with zirconium - "Equiv. of zirconium = $\frac{90}{4}$ = 22.5 is close to the equiv. of eka-aluminium and eka-molybdenum since Ea = $\frac{67}{3}$ = 23 and Emol. = $\frac{Mo + W}{2}$ = 140 and $\frac{140}{6}$ = 23.3. And consequently perhaps there are admixtures in zirc.".[210]

In February 1871 table 31 (P8) was published, containing estimated atomic-weight values for all of the missing elements which Mendeleev considered to belong to the region between Ba and Ta (the assumed element of atomic weight 153 was included in this table twice, in the same way as were its analogues Cu, Ag and Au):

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[209] Ibid., pp. 53-4 (PLBA, 99). By the term "cerite metals" Mendeleev here seems to be referring not only to what were usually called "cerite" elements, but also to the so-called "gadolinite" elements - i.e. to the "rare-earth" elements in general (see Ch. VII, section A).

[210] Sc.Ar., 290-1. Concerning the dating of this manuscript, see Sc.Ar., 305. The element which Mendeleev here calls "eka-molybdenum" had been assigned an atomic weight of "?143" by him in table 17 (M11) (see Fig. VI - 1, above); later, in tables 31 (P8) and 38 (P14) he was to give it an atomic weight of 146 (see Fig. VI - 3, below).

I	II	III	IV	V	VI	VII	VIII
Cs=133	Ba=137	?138=La?=Di?(144)	Ce=140(138?)	142	146	148	150 151 152 153
153	158	160	162	164	166	168	
175	177	?178=Er?(169)	?180=Di?=La(187)	Ta=182	[etc., see Fig. VI-4]		

Fig.VI-3.

The same estimated atomic-weight values were subsequently included in the very similar table 38 (P14), published in 1873 in Part II of the 2nd edition of Principles of Chemistry (R.).

In November 1871 Mendeleev's long article on The periodic lawfulness of the chemical elements (G.) was published. Having presented in this article his detailed predictions for "eka-boron", "eka-aluminium" and "eka-silicon", and having discussed to a much lesser extent the expected properties of "dvi-boron", Mendeleev went on to say -

> The examples which have been considered indicate clearly the methods by means of which it is possible to predict the properties of unknown elements on the basis of the periodic law; I shall therefore pursue no further the subject of the properties of missing elements. The most interesting would be the discovery of the properties of the following elements: eka- and dvi-caesium, Ec = 175 and Dc = 220;[211] eka-niobium En = 146 and eka-tantalum Et = 235;[212] and the analogues

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[211] Mendeleev mentions the unknown elements "eka-caesium Ec = 175" and "dvi-caesium Dc = 220" also earlier in this article (Op.cit., pp.196-7; PLBA, 150). The atomic weight 175 given by Mendeleev in this article for "eka-caesium" is the same as he gave for this element in tables 31 and 38 (see Fig. VI - 3). The element "dvi-caesium" is considered below, in sub-section e).

[212] The value En = 146 given here should be contrasted with the value 142 given by Mendeleev for the atomic weight of this element in tables 31 and 38 (see Fig. VI - 3); in tables 31 and 38 it is the element "eka-molybdenum" which is assigned an atomic-weight value of 146.

In 1881 the Czech chemist Brauner, in a letter to Mendeleev, suggested that perhaps the element "neptunium" which Hermann had claimed to have discovered about 5 years earlier was in fact the element "eka-niobium En = 146" which Mendeleev had mentioned in 1871 in The periodic lawfulness of the chemical elements (G.) (see Bibl.38, pp.26-7). This suggestion was not adopted by Mendeleev.

The element "eka-tantalum" is considered below, in sub-section e).

> of manganese, e.g. eka-manganese Em[214] = 100, tri-manganese Tm = 190.[213] The lack of the entire 9th series[214] and even of almost an entire large period (beginning from Ce = 140) should, however, hardly be attributed solely to chance, and it may be that there are reasons in the nature of the elements.[215, 216]

Mendeleev here acknowledges only "almost" an entire large period to be missing, beginning from Ce = 140, because in this article he suggests that Er and La occupy the two places immediately preceding Ta = 182, as indicated in the tables 35 (P11) and 36 (P12) which accompany the article. Despite his reference in the above-quoted passage to "eka-niobium En = 146" and "eka-...-caesium, Ec = 175", none of the places between Ce = 140 and Er = 178 in tables 35 (P11) and 36 (P12) is marked with anything more than a dash.

In manuscript additions to an off-print of The periodic lawfulness of the chemical elements (G.; 1871) Mendeleev indicated that he considered "eka-tellurium" to have an atomic weight of 173 (see earlier, p.345; contrast the value 166 given for the atomic weight of this element in tables 31 and 38).

In his article On the history of the periodic law (G.; 1880) Mendeleev appended the following footnote to the unoccupied place in table 45 (P20) corresponding to the element which according to his system of nomenclature would be called "eka-cadmium": "In this place Carnelley (Philos. Magaz., 1869 [sic], p.312, Oct.) puts norwegium, Ng = 146, discovered by Dahll [sic][217]." Mendeleev himself did not use the term "eka-cadmium" at this stage. Nine years later, however, in the 5th edition of Principles of Chemistry (R.; 1889), he did come to talk of "eka-cadmium", predicting a fairly detailed list of properties for this element and again suggesting its identity with Dahl's "norwegium":

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[213] Mendeleev here appends a footnote suggesting that perhaps Em is Ru, and Tm is Os (see earlier, p.385).

[214] In this article Mendeleev had come to use his later (complete) system of numeration of the series - see table 36 (P12).

[215] In the original Russian manuscript draft of this passage the final sentence was longer than in the published German version, ending with the words, "... and it may be that there are, in the nature of the elements, reasons which do not allow equilibrium and undecomposability for the formation of elements having atomic weights of about 150-175" (see Sc.Ar., 446).

[216] The periodic lawfulness of the chemical elements (G.; 1871), p.205 (PLBA, 156-7).

[217] Zur Geschichte des periodischen Gesetzes, Berichte, 13 (1880) 1796-1804; p.1804 (PLBA, 406). The article by Carnelley to which Mendeleev here refers appeared in 1879, not in 1869. On the "discovery" and properties of "norwegium", see: T. Dahl, Chem. News, 40 (1879) 25; Compt. Rend., 89 (1879) 47; Berichte, 12 (1879) 1731; Berichte, 13 (1880) 250, 1861.

I consider it appropriate to turn attention to the absence, according to the periodic system, of an element (eka-cadmium) between cadmium and mercury. But because in the 9th series not a single element is known, then perhaps the whole of this series comprises elements which are unable to exist. However, until this has somehow been proved we may conclude that the properties of eka-cadmium will represent a mean between those of Cd and Hg. It should have an atomic weight of about 155, and form an oxide EcO and an unstable suboxide Ec_2O, both of which should be weak bases which readily give double and basic salts.[218] The volume of the oxide will be approximately 17.5, because CdO has a volume of about 16, and HgO of 19. The density of the oxide will therefore be approximately 171:17.5 = 9.7. The metal should be readily fusible, oxidising with calcination; it should be of grey colour, with a specific volume of about 14 (Cd = 13, Hg = 15), and therefore its specific gravity (155:14) will be approximately 11. Such a metal is unknown. But in 1879 Dahl, in Norway, discovered - on Otterøy island, not far from Krogerø, in a vein of well-known spar in a nickel ore found there - the presence of a new metal which he called norwegium, and which shows some resemblance to eka-cadmium. Little of the ore was found, the experiments were not extensive, the first results were insufficient, and complete purity of the extracted metal was not achieved; and therefore the properties cited for norwegium should be looked upon as approximate, and liable to change appreciably with further study. A solution of the burnt mineral in acid was twice precipitated with H_2S and again burnt; the oxide obtained was easily reduced. When the metal was dissolved in very dilute aqueous HCl, boiling the solution gave a basic salt, freed moreover from copper, which remained behind in solution. The reduced metal had a density of 9.44, it melted at 254°, and it was easily oxidised; if the composition of the oxide is NgO, then Ng = 145.9. The hydroxide dissolved in alkalis and K_2CO_3. In any case, if norwegium is not a mixture of other metals it belongs to an odd (uneven) series, because the heavy metals of the even series are difficult to reduce, whereas norwegium is easily reduced. Brauner considers that norwegium oxide is Ng_2O_3, atomic weight Ng = 219,[219] and places norwegium in group IV, series 11,[220] and it should then form a weakly acidic higher oxide NgO_3.

A modified version of this passage still remained in the 7th (1902-3) edition of Principles of Chemistry (R.). In this 7th edition the second sentence of the passage had been extended, thus - "But because in the 9th series not a single element is known, then perhaps the whole of this series comprises elements which are unable to exist, or else it may be that the metals of the rare earths are placed here".[221] Also, although Mendeleev still

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[218] In tables 31 (1871) and 38 (1873) Mendeleev had assigned an atomic weight of 158 to the element "eka-cadmium" (see Fig. VI - 3). In his Annalen paper of 1871 he had used the symbol "Ec" to denote "eka-caesium" (see above, p.395).

[219] This is the place of "dvi-tellurium" - see sub-section e), below.

[220] Pr.Ch., R-5 (1889) 488, n.27.

[221] Pr.Ch., R-7 (1902-3) Ch. XVI, n.27. The underlining is mine, not Mendeleev's.

referred to "norwegium", he now gave fewer details of the properties which had been claimed for this "element", and added, "I have not heard more about it, and possibly it is not a new element after all".[222] In the 8th (1906) edition of Principles of Chemistry (R.) the corresponding passage was reduced to only the first two sentences of the version given in the 7th edition, i.e. the predicted properties of "eka-cadmium", and all references to "norwegium", were now omitted.[223]

In 1898, in an article on The periodic lawfulness of the chemical elements (R.), Mendeleev discussed briefly the question of the likely properties of an unknown higher analogue of iodine:

> ... we cannot but point out that for unknown elements which are not adjacent to - or, so to speak, surrounded by - known elements, it is impossible to give such detailed predictions of properties as we could for Ge, Ga and Sc. We may, for example, say that with the discovery of a halogen X with atomic weight greater than that of iodine, it will form KX, KXO_3, etc., that its hydrogen compound will be a gaseous very weak acid, and that its atomic weight will be either about 170 or 215; but neither for a halogen of the 9th series, nor for a halogen of the 11th series, can we already foresee many properties in detail, because there are no neighbouring well-known elements.[224]

The atomic weight of about 170 predicted by Mendeleev in this passage for the element which we could call "eka-iodine"[225] is close to the value 168 which he had predicted much earlier for this element in tables 31 and 38 (see Fig. VI - 3).[226] No halogen of such an atomic weight actually exists.

With the incorporation into Mendeleev's periodic table in the early 20th century of the "zero" group of inert gases a new place was introduced into the region of the table between Ba and Ta, corresponding to an unknown inert gas which we could call "eka-xenon"[227] (see tables 57, 58, 60-64). This element "eka-xenon" does not in fact exist, its prediction being yet another consequence of Mendeleev's erroneous extension of the periodic system into the

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[222] Ibid.

[223] See Pr.Ch., R-8 (1906) n.429.

[224] Bibl.11, vol. 23, half-vol. 45, 1898, p.320 (PLBA, 263).

[225] Mendeleev himself did not use the term "eka-iodine".

[226] Concerning the halogen of atomic weight ca. 215 suggested by Mendeleev in this passage of 1898, see sub-section e), below.

[227] Mendeleev himself did not use the term "eka-xenon".

region between Ba and Ta; the actual next highest existing analogue of xenon, viz. radon, corresponds to what in Mendeleev's table would be "dvi-xenon".[228]

e) Elements between Ta and U

Strictly speaking, the heading of this sub-section relates only to the period after Mendeleev's adoption in 1870 of an atomic-weight value for uranium of ca. 240 instead of the value 116 or 120 which he had assumed earlier. But although before this time there was no region "between Ta and U" beyond Ta = 182 in Mendeleev's periodic tables, the indications in these early tables concerning missing elements with atomic weights greater than that of Ta are nevertheless also considered in the present sub-section, because in certain cases they represent direct precursors of later predictions by Mendeleev which do indeed concern elements coming strictly "between Ta and U". To this precursory period of about a year from March 1869 belongs the first of three stages which we shall distinguish in the history of Mendeleev's views concerning missing elements belonging "between Ta and U". The second stage began in the summer-early autumn of 1870, when Mendeleev drew up his earliest known periodic table to include uranium with an atomic weight of ca. 240, viz. table 17 (M11), and extended right up to the end of the 19th century; the third stage emerged in the early 20th century.

In table 3 (M3) and its published counterparts tables 8 (P1) and 9 (P2), and in table 6 (M6), the place immediately following W is occupied by Pt. In tables 5 (M5), 10 (P3), 11 (M8) and 15 (P6) on the other hand there is an unoccupied place between W and the platinum elements; and insofar as this represents a missing element immediately following W in the periodic table, belonging to what later came to be called "group VII", it can be seen as an early anticipation by Mendeleev of the existence of the element rhenium. In table 10 (P3) we even find an estimated atomic-weight value of 190 for this missing element (cf. Re = 185, taking H = 1).[229]

Many of Mendeleev's periodic tables of 1869 have unoccupied places marked for elements with atomic weights greater than those of the platinum elements. However, since the placings given in these tables for the known elements included in this region (Au, Hg, Tl, Pb, Bi) are mostly wrong, some of the gaps actually correspond to the correct places of known elements. Exceptions are provided by the two gaps included for elements missing from

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[228] See sub-section e), below.

[229] Rhenium was discovered in 1925.

"group VI" and "group VII", corresponding respectively to the elements polonium and astatine. In tables 6 (M6) and 10 (P3) estimated atomic-weight values are given for the element corresponding to astatine, viz. "226?" and "220" respectively (cf. the value 208.3, taking H = 1, for the mass number of the most stable isotope of At).[230]

In table 17 (M11), drawn up in the summer-early autumn of 1870, Mendeleev for the first time extended the periodic table beyond the row which immediately follows the Ta - W row in the short-form arrangement, introducing a further row in order to include Th = 231 and U = 240 (which he placed respectively in "group IV" and "group VI"). None of the resulting 7 unoccupied places between W and U in table 17 (M11) belongs to an element which was known at the time, Mendeleev by now having come to classify Au, Hg, Tl, Pb and Bi correctly. Of these 7 places, the one immediately following W, corresponding to rhenium, contains the entry "x = 190"; the other six unoccupied places in this region of table 17 (M11) - which have turned out to belong to the elements polonium, astatine, francium, radium, actinium and protoactinium[231] - are completely blank. From the time of his compilation of table 17 (M11) right up to the end of the 19th century the unoccupied places recognised by Mendeleev for the region of the periodic table between Ta and U were just those very same 7 unoccupied places as are seen in this region of table 17 (M11). There appear to have been only 5 tables of this period where Mendeleev gave estimated atomic-weight values for one or more of these 7 missing elements: the manuscript table 20 (M14), dating from the autumn of 1870, contains the entry "? = 190" in the place immediately following W (i.e. corresponding to Re); and the four published tables 31 (1871), 38 (1873), 39 (1875) and 41 (1877) each contain one or more such estimated values (see below).

In his article A natural system of the elements (R.; written late 1870, publ. Feb. 1871) Mendeleev predicted certain properties for 5 of the 7 elements for which he had left gaps between Ta and U in the periodic table accompanying this article, table 30 (P7), viz. for the 5 missing elements corresponding to polonium, francium, radium, actinium and protoactinium:

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[230] Polonium was discovered in 1898, astatine in 1940.

[231] Radium was discovered in 1898, actinium in 1899, protoactinium in 1917, and francium in 1939.

Among the heavy metals, i.e. those having a large atomic weight, we can expect an element analogous to tellurium, having an atomic weight greater than that of bismuth. It should possess completely metallic properties, with the tendency to give an acid of the composition and properties of H_2SO_4 but which acts as an even stronger oxidising agent than telluric acid. The oxide RO_3 of this element (which stands in the place VI - 9 [sc. in table 30 (P7)]) should, certainly, already be quite an energetic base, like the oxide of bismuth; so that for this oxide of composition RO_3 we already cannot expect the acidic properties which are still observed in tellurous acid. This element certainly should also form organometallic compounds; it probably does not give hydrides, because as atomic weight increases, and with increase in basic metallic character, the tendency to combine with hydrogen decreases, as is observed with the transition from chlorine to bromine to iodine.[232] Then in the tenth series [sc. in table 30 (P7)] we can again expect basic elements belonging to groups I, II and III; they should have atomic weights of about 210-230. The first of these elements should form an oxide R_2O, the second, RO, and the third, R_2O_3; the first will resemble caesium, the second, barium, and the oxides of all of them should certainly possess the character of very energetic bases, because in this 10th series even thorium in its oxide ThO_2 already possesses distinctly basic properties, and even uranium, which also stands in the same series, still shows a clearly basic character in its oxide UO_3.[233] Between thorium and uranium in this series we can further expect an element also of basic character, although weakly developed, with an atomic weight of about 235. This element should form a highest oxide R_2O_5, like Nb and Ta to which it should be analogous. Perhaps in the minerals which contain these elements a certain amount of a weak acid formed by this metal will also be found.[234, 235]

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[232] The element which actually follows immediately after bismuth in the periodic table, viz. polonium, has an atomic weight (taking H = 1) of 208.3, that of Bi being 207.3. Polonium is indeed an analogue of tellurium, its chemical properties having been investigated mainly by using tellurium as "carrier". Polonium also resembles bismuth in certain of its chemical properties - for example, it has been shown (F.A. Paneth, 1918) that polonium does in fact form a volatile hydride, the properties of which are similar to those of bismuth hydride (the latter hydride is, however, more stable).

[233] The atomic weights, referred to H = 1, of francium, radium and actinium are 221.2 (mass number of most stable isotope), 224.2 and 225.2 respectively. Francium is readily co-precipitated with rubidium or caesium perchlorate or chloroplatinate as "carrier", i.e. its properties correspond to those of an alkali metal; radium is an analogue of barium; and actinium shows a close resemblance to lanthanum in its properties.

[234] The element between Th and U in the modern periodic table, viz. protoactinium, actually has an atomic weight of 229.2 (H = 1), which is lower than that of Th (230.2): Th and Pa constitute one of the 4 pairs of elements in the periodic table where a decrease of atomic wieght occurs with an increase in atomic number. Protoactinium in its properties shows a strong analogy with tantalum, e.g. its highest (and most stable) oxide is Pa_2O_5. However, as Pa (IV) it also shows a strong horizontal analogy with Th and U (IV). Pa was discovered in the uranium mineral, pitchblende.

[235] Op.cit., pp. 54-5 (PLBA, 99-100).

In table 31 (P8), which appeared in February 1871, Mendeleev gave estimated atomic-weight values for all 7 of the elements which he assumed to be missing from the region between Ta and U:

I	II	III	IV	V	VI	VII	VIII
	[see Fig. VI-3]			Ta=182	W=184	190	Os=193 Ir=195 Pt=197 Au=197
Au=197	Hg=200	Tl=204	Pb=207	Bi=208	210	212	
220	225	227	Th=231	235	U=240	[etc.]	

Fig. VI-4.

The same values were again given in table 38 (P14), in 1873. In his article on The periodic lawfulness of the chemical elements (G.; publ. Nov. 1871) Mendeleev referred to "dvi-caesium Dc = 220" (corresponding to the unknown francium), "eka-tantalum Et = 235" (protoactinium) and "tri-manganese Tm = 190" (rhenium), suggesting in a footnote that perhaps "tri-manganese" is in fact osmium (see earlier, pp.395-6 and 385). In table 39 (P15), published in 1875, we find the entry "?190" for the element "tri-manganese"; and table 41 (P16), 1877, has the entries "?190" and "?237" for "tri-manganese" and "eka-tantalum" respectively. The value 237 given in table 41 for the atomic weight of "eka-tantalum" is even further removed from the actual atomic-weight value of protoactinium (229.2) than had been Mendeleev's earlier estimate of the atomic weight of "eka-tantalum" (235).

In his Faraday lecture, 1889, Mendeleev predicted the properties of "dvi-tellurium" (corresponding to polonium) in some detail:

> I foresee a number of elements which are still unknown, but not with the same certainty as before [sc. as for "eka-boron", "eka-aluminium" and "eka-silicon"]. I shall give one example, but I see it only dimly. In the series containing Hg = 200, Tl = 204, Pb = 206 and Bi = 208, I envisage (in the place VI - 11) an element analogous to tellurium, which I shall call dvi-tellurium Dt. This will be seen to have an atomic weight of about 212, and a tendency to form DtO_3. In the free state the simple body should (if it really exists) be an easily fusible, crystalline, difficultly volatile, grey-coloured metal, with

a specific gravity of about 9.3,[236] and tending to oxidise to DtO_2, which will be equally endowed with weakly acidic and weakly basic properties. This dioxide should, with active oxidation, form an unstable higher oxide DtO_3, which in its properties will be reminiscent of PbO_2, Bi_2O_5. Dvi-tellurium hydride, if it actually exists, will be still less stable than H_2Te, but its existence will nevertheless probably be reflected not only in the easy reduction of dvi-tellurium compounds, but also in the tendency of the metal to give characteristic definite alloys with other metals.[237]

In 1898 Mendeleev talked of an unknown halogen of atomic weight ca. 215, occupying the place VII - 11 in the short-form periodic table (see earlier, p.398). This unknown halogen corresponds to the element astatine.

The incorporation of the "zero" group of inert gases into Mendeleev's periodic table in the early 20th century led to his recognition of a new unoccupied place in the region between Ta and U, viz. the place 0 - 12, corresponding to a missing inert gas which we could call "dvi-xenon"[238] (see tables 57, 58, 60-64). This place actually belongs to the element radon; but Mendeleev never suggested that the newly-discovered "emanation" - as radon was called at the time - was in fact a new inert gas occupying this vacant place.[239] At the same time as he first included the "zero" group in his periodic system Mendeleev also introduced radium into the system, as "Rd = 224" (later as "Rd = 225") in its rightful place as an analogue of barium in the same series of the short-form table as Th and U, i.e. in the previously unoccupied place II - 12. The remaining 6 of the 7 places which had been unoccupied between Ta and U in Mendeleev's periodic tables from 1870 up to the end of the 19th century were still vacant in his tables of the early 20th century.[240] Consequently, with the new place corresponding to that

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[236] The specific gravity of polonium metal is 9.3.

[237] PLBA, 226, footnote.

[238] Mendeleev himself did not use the term "dvi-xenon".

[239] For certain comments by Mendeleev concerning "emanation" see pp. 98-9 and 464.

[240] Although polonium and actinium had, like radium, been discovered by the end of the 19th century, unlike the better-characterised radium they were never placed in the periodic table by Mendeleev. In the 8th (1906) edition of Principles of Chemistry (R.) Mendeleev wrote: "So far three such elements [sc. radioactive elements other than Th and U] have been recognised: radium, which resembles barium, polonium, which resembles bismuth, and actinium, which resembles thorium, ... but of these only radium has been obtained in a relatively pure state" (op.cit., p.734; PLBA, 525).

of radon in group 0, Mendeleev's tables of the early 20th century still contained 7 unoccupied places between Ta and U, although these were not quite the same 7 places as had been previously unoccupied in this region of the table.

f) Elements coming after U; the question of the upper limit of the periodic system

Before Mendeleev's adoption in 1870 of an atomic-weight value for uranium of ca. 240 rather than 116 or 120, the element with the highest atomic-weight value in his periodic table was Bi (210). At this stage the question of the upper limit of the table had not yet been raised by Mendeleev. He seems to have first expressed his concern with this question of the upper limit in his article A natural system of the elements (R.; written late 1870, publ. Feb. 1871):

> With the tenth series [sc. series 10 in table 30 (P7)] the known elements come to an end. And whereas in the series of typical elements we find many acidic elements, an occurrence not repeated in the subsequent rows, when we come to the tenth series we find many basic elements, an occurrence similarly not encountered in the other rows - from which there are grounds to conclude that here we are already close to the end of the possible forms of elementary combinations [sc. elements]. This assumption is strengthened by the fact that the typical elements differ in atomic-weight value from the elements of the same group in the first series [sc. series 1 in table 30 (P7)] by approximately 16, whilst in subsequent rows this difference attains 25 and even more, but then again is apparently lower between the corresponding elements of the last rows.[241]

Mendeleev's remark in this passage that in series 10 of table 30 (P7) we find "many" basic elements seems somewhat strange when this series actually contains only two known elements, viz. Th and U. But what he undoubtedly has in mind is that since uranium in group VI is a basic element, then all of the elements in the earlier groups in this series (among which is the basic thorium) will also be basic, in accordance with the general tendency for the earlier groups to be more basic than the later groups. His claim that the predominant basicity of the series containing Th and U provides grounds for concluding that this series is near the upper limit of the possible elements appears to be founded upon the attractive simplicity of the idea that the periodic table comes to an end with the completion of a transition through the rows from the predominant acidity of the "typical" series to a series showing a corresponding predominant basicity - i.e., upon the attraction of a sort of acidity/basicity inversion symmetry for the short-form table. The other factor cited by Mendeleev in the above passage as providing grounds for belief that the thorium-uranium row in the short-form periodic table is near

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[241] Op.cit., p.55 (PLBA, 100-101).

the upper limit of the table is also one whose attraction lies in symmetry considerations, viz. in the idea that the atomic-weight differences between corresponding elements (i.e. in the same group) of the "typical" series and series 1 in table 30 (P7), and of the penultimate and final rows in this table, are both appreciably lower than the differences between adjacent rows in the central region of the table. But attractive though this idea may be, Mendeleev's statement that in fact the difference "between the corresponding elements of the last rows" is lower than for the preceding rows is, unaccountably, simply not in accordance with the scant evidence provided in table 30 (P7).

In his article The periodic lawfulness of the chemical elements (G.; 1871) Mendeleev again discussed the question of the upper limit of the periodic system. He referred once more to the predominant basicity of the heaviest known elements, and cited also certain other factors as being relevant to the question, but he now no longer mentioned the atomic-weight differences between the rows of the short-form table:

> Is the number of elements limited or unlimited? Judging from the limitedness and, so to speak, exclusiveness of the system of the elements which are known at present; from the fact that these same elements exist in meteorites, and on the sun and stars; from the fact that at high atomic weights the acidic properties of the elements disappear; and from the fact that the majority of elements of high atomic weight give heavy metals which are oxidised with difficulty, we may think that the number of elements available to us is very limited, and that if there exist a few new heavy elements within the mass of the earth then their number and quantity will be very limited.[242]

It is not clear just in what way Mendeleev considered limitedness in the number of possible chemical elements to be indicated by the metallic nature of the free forms of elements of high atomic weight and the relatively low tendency of these metals to be oxidised; he does not appear to refer to this point elsewhere. Possibly he felt that such properties of the heaviest elements should make these elements fairly easily discoverable, and that it was therefore unlikely that there should remain many still undiscovered.

The only further comments by Mendeleev with some bearing upon the question of the upper limit of the periodic table appear to be certain remarks of the early 20th century where he gives the impression that while he recognises that uranium is only the heaviest of the known elements, and not necessarily the heaviest possible element, he feels nevertheless that this element is very near the upper limit of possible elements. For example, in the 8th (1906) edition of Principles of Chemistry he expressed the opinion that the association between uranium and the inert gases (especially helium)

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[242] Op.cit., pp. 205-6 (PLBA, 157).

and the phenomenon of radioactivity is "linked in some still deeply hidden manner with the extremeness (krainost') of uranium itself in the evolution of the elements".[243]

The only known attempts by Mendeleev to predict atomic-weight values for elements beyond uranium (U = 240) in the periodic table are to be found in the short-form tables 31 (P8) (1871) and 38 (P14) (1873). In both these tables the uranium row is extended five places beyond that of uranium up to that of a higher analogue of Au in group VIII, the estimated atomic-weight values for the five missing transuranium elements being given as 245, 246, 247, 249 and 250 respectively. In many of Mendeleev's other tables one or more places after that of uranium are marked with a dash, suggesting that these places might belong to unknown elements. There was, however, clearly no definite idea in Mendeleev's mind about the number of such elements: the maximum number of places which he marked for transuranium elements varied according to the form of the periodic table, so that whereas no more than five places beyond uranium were marked in the short-form tables, in the long-form tables eleven such places were often marked (see, for example, the long-form tables 32, 43 and 56). Mendeleev showed a lesser tendency to mark transuranium places in his later periodic tables.

It is perhaps of interest to note that before the incorporation of group 0 into his periodic system in the early 20th century, the total number of places indicated in the long-form tables in which Mendeleev had marked places for transuranium elements was exactly 100 (see, for example, tables 32, 35 and 52). Mendeleev did not comment upon this, however, let alone claim it as grounds for predicting a limit of exactly 100 elements.

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[243] Pr.Ch., R-8 (1906) 732 (PLBA, 522).

CHAPTER VII

MENDELEEV ON THE RARE-EARTH ELEMENTS AND INERT GASES

A. Introduction

The rare-earth elements and the inert gases were both included by Mendeleev in the broad class of what he referred to as "rare elements".[1] There is, however, a much more interesting link between these two sets of elements in relation to Mendeleev's work than merely this common designation "rare": both sets of elements provided a strong test for Mendeleev's periodic classification of the elements. The problem of the rare-earth elements was one which was present, and which continued to grow, throughout the period of Mendeleev's involvement with the classification of the elements; the problem of the inert gases on the other hand emerged only in the mid-1890's, and had been solved within 5 or 6 years.

The history of the discovery of the rare-earth elements is extremely complicated, as would indeed be expected for such a large group of elements of closely similar chemical properties occurring in nature in the same few minerals.[2] It begins in the 18th century with the discovery of the minerals "ochroite" (later called "cerite") (1751) and "ytterbite" (later "gadolinite") (1788). In 1794 Johann Gadolin isolated from ytterbite a "new earth" which he called "ytterbia", soon to be re-named "yttria" by Ekeberg. In 1803 Berzelius and Hisinger, and independently of them Klaproth, discovered in ochroite a new earth which was given the name "ceria". In 1839 Karl Mosander isolated a new earth, which he called "lanthanum", from the "cerium" of 1803. Two years later he separated this "lanthanum" into two parts - lanthanum and "didymium"; and in 1843 he separated the old "yttria" into three components - yttria, "terbia" and "erbia". During the course of the subsequent 20 years or so a terminological confusion led to Mosander's "terbium" coming to be known as "erbium", and vice versa. Also, at this time Mosander's "erbium" - i.e., the substance which others now usually referred to as "terbium" - was considered by most chemists to be a

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[1] The class of "rare elements" for Mendeleev embraced not only the "rare-earth elements" (among which he included, in addition to the lanthamide elements, not only Sc and Y but also Th) and the inert gases, but also some ordinary transition elements such as V and Nb, and sometimes certain other elements, e.g. Cs (see, for example, his comments in an article in Bibl.11, 1904: PLBA, 417-8). Most of these elements are in fact not particularly rare, and some are even abundant; but they tend not to occur in any great concentrations terrestrially.

[2] On the history of the discovery of the rare-earth elements see, for example: Bibl.130; Bibl.119; and the article "The rare earths" (in Russian, transl. from the original French) by G. Urbain, dated 22 Feb., 1926, given on pp. 631-671 of volume 2 of the 9th Russian edition (1st posthumous edition) of Mendeleev's Principles of Chemistry, 1928.

doubtful element, probably a mixture of other, known, elements. However, as a result of Marignac's researches of 1878 on the rare earths, this "terbium" (Mosander's "erbium") eventually came to be generally acknowledged as a genuine element, being in fact the element which is still known as "terbium".

The state of discovery of the rare-earth elements by 1869, when Mendeleev drew up his first periodic system, was therefore as follows: three "cerite" elements were known and generally accepted - cerium, lanthanum and didymium; and two "gadolinite" elements - yttrium and erbium - were generally recognised, with terbium considered by some as a possible third.

The discovery of the periodic law, the development of spectroscopic analysis (Bunsen and Kirchhoff, 1859-60), and improvements in chemical fractionation techniques all contributed to the rapid advances which were made in the field of rare-earth chemistry during the last quarter of the 19th century and in the early 20th century. This was a period of great activity, with not only the genuine discovery of many new rare-earth elements but also a (probably even greater) number of what turned out to be false "discoveries". Prominent in the field of rare-earth research at this time were Marignac, Clève, Delafontaine, Lecoq de Boisbaudran, Lawrence Smith, Brauner, Auer von Welsbach, Crookes, Demarçay and Urbain.

A much simplified schematic outline of the history of the discovery of the rare-earth elements is given below in Fig. VII-1. Modern chemical symbols are used throughout, from the earliest "yttria" (1794) and "ceria" (1803) onwards, corresponding to the names given at the time to the substances discovered.[3] "Final" discoveries, where an element was obtained in a state from which no further separation of new rare-earth elements was later made, have been indicated by giving the symbol of the element in heavy print.

In 1868 a new yellow line was observed in the solar spectrum by Janssen, leading Frankland and Lockyer to postulate the existence on the sun of a hitherto unknown element which they named "helium". Early in 1895 Ramsay extracted from the uranium mineral cleveite a gas which was shown to give a spectrum identical to that of the solar "helium" (Hillebrand had already obtained a sample of this gas from cleveite in 1889, but had characterised it as nitrogen). Later in 1895 helium was found by Kayser to occur in extremely small amounts in the earth's atmosphere.

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[3] Gadolin's "ytterbia" (1794), which soon came to be called "yttria", has been given the symbol Y, not Yb. Didymium is given the symbol Di, in accordance with the practice of the time.

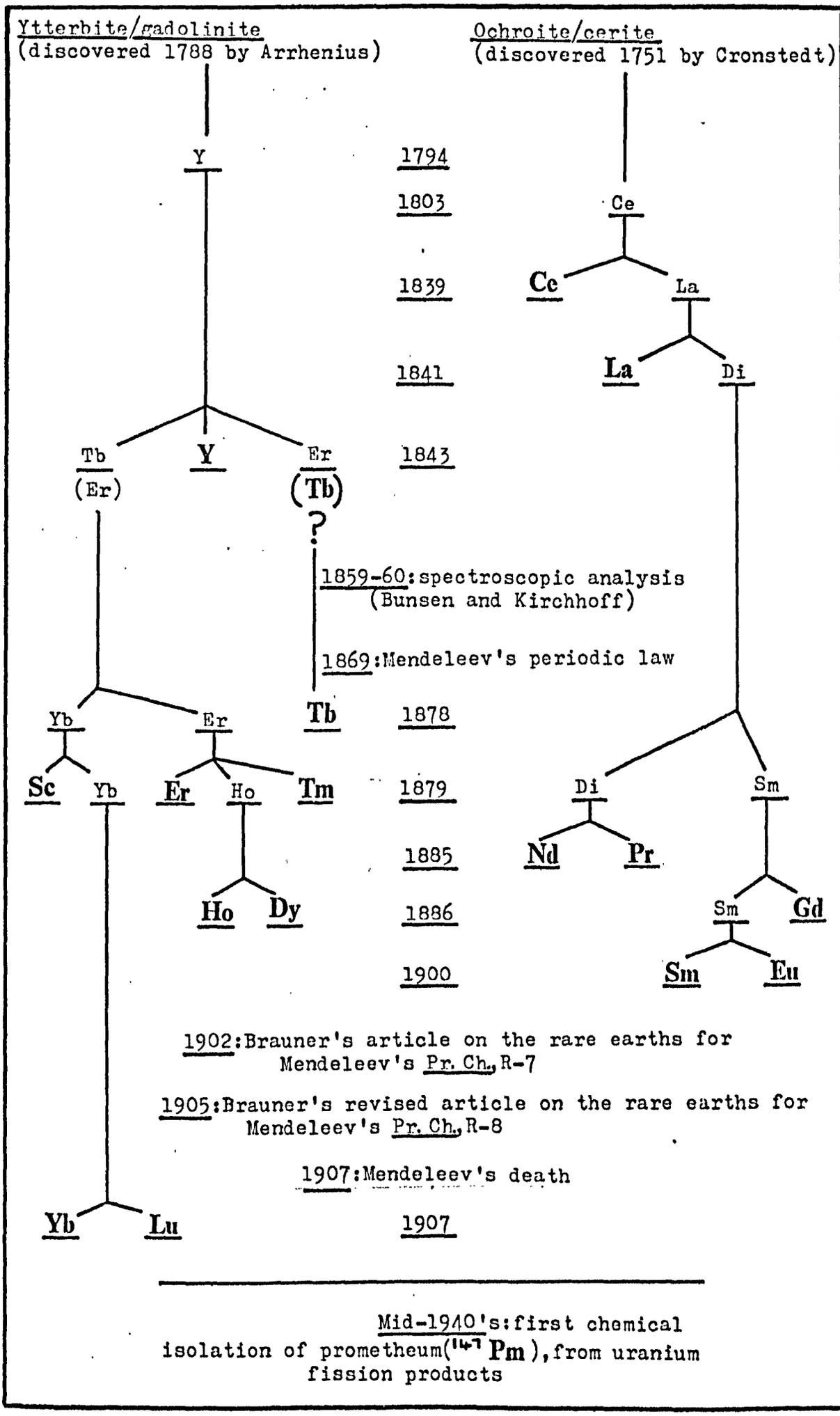

Fig.VII-1.

History of discovery of the rare-earth elements.

The first of the inert gases to be discovered on the earth was argon, by Rayleigh and Ramsay in 1894: this new gas was isolated from the atmosphere after experiments had shown a discrepancy between the densities of atmospheric nitrogen and chemically-derived nitrogen (from compounds such as ammonia, nitric oxide, nitrous oxide, etc.). More than 100 years earlier, in 1775, Cavendish had obtained a gaseous residue after the conversion of "phlogisticated air" (nitrogen) to nitrous oxide by electrical sparking of air with excess oxygen over potash, but the significance of this result had remained obscure until the experiments of Rayleigh and Ramsay in the 1890's.

The "argon" isolated from the atmosphere by Rayleigh and Ramsay in 1894 still contained small amounts of other inert gases. In 1898 Ramsay and Travers separated the new element neon from such "argon", by fractional distillation of the liquid; later in the same year they discovered also krypton and xenon, by further fractionation of the less volatile fractions of liquid air. Radon was discovered during the early years of the 20th century - first by Dorn in 1900 - as "emanation" from various radioactive substances.[4]

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[4] On the history of the discovery of the inert gases see, for example, Bibl. 28 (pp.3-20: "Historical remarks on the discovery of argon, the first noble gas", by E.N. Hiebert), Bibl. 117 and Bibl. 130.

B. Mendeleev's views on the rare-earth elements

Mendeleev's attempts at placing rare-earth elements in his periodic system from the time of his first "attempt at a system" (March 1869) to the time when he eventually drew up his "natural system" (Nov./Dec. 1870) are indicated below in Fig. VII-2.[5]

Although Mendeleev did include yttrium, lanthanum, didymium, cerium and erbium (and also an unknown element "? = 45") in his "attempt at a system", tables 3, 8 and 9, he did so only tentatively and unsatisfactorily at the edge of the table.[6] Except for the case of erbium, the atomic weights given in Mendeleev's "attempt at a system" for these rare-earth elements - viz. Er = 56?, Yt = 60?, Ce = 92, La = 94 and Di = 95 - correspond, in accordance with the accepted practice of the time, to the formula-type RO for the usual oxides of these elements. The value given for erbium is simply its equivalent weight.[7]

In table 11 (M8) (spring 1869) Mendeleev included only cerium of the rare-earth elements, placing it (as "Ce = 92") in association with the elements of the palladium family in that region of the table which later came to be designated "group VIII". A tendency to classify cerium and its analogues near the palladium elements had already been shown in the rough manuscript table 2 (M2) (March 1st, 1869); and in his first article on the periodic law, Correlation of properties (R.; written March 1869, publ. May 1869), Mendeleev associated cerium and its analogues with the iron, palladium and platinum families in his discussion of the problem of how best to arrange all of the elements into a single coherent classificatory system:

> The proposed system of the elements [sc. the "attempt at a system", table 9 (P2)] certainly cannot be considered as final ... Many questions arise in connection with the arrangement of all of the elements into a single integral system, but the most interesting question seems to me to be that of the arrangement of those elements which resemble iron, cerium, palladium and platinum, because here we have elements of a similar nature possessing similar atomic weights.[8]

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[5] It will be noticed that Mendeleev used the symbol "Yt" for yttrium in his early periodic tables. He came to adopt the symbol "Y" for this element in 1881.

A chart somewhat similar to Fig. VII-2 is given by Kedrov in Sc.Ar., 812-5.

[6] Mendeleev at this time was dubious about the existence of terbium. An expression of this doubt is to be found, for example, in his Annalen paper of 1871, p.194 (PLBA, 148).

[7] About 12 months later (March 1870), in the 3rd instalment of the 1st edition of Principles of Chemistry, Mendeleev cited Bunsen's value of 112 for the atomic weight of erbium, corresponding to the formula ErO for the usual oxide (PLSM, 290).

[8] Op.cit., pp. 73-4 (PLBA, 28).

"Attempt at a system" — Table 3 (M3) [Tables 8 (P1) and 9 (P2)]	F Cl Br J Li Na K Rb Cs Tl Ca Sr Ba Pb ?=45 Ce=92 ?Er=56? La=94 ?Yt=60? Di=95 ?In=75·6? ?Th=118?
Table 11 (M8)	? | Cr Mn Fe Ni Co Br ? | Mo Rh Ru Pl Ce=92 J
Table 16 (M10)	C Si Ti x=74 Zr Sn B Al x=44 x=68 CeLaDi92 In=113·4 Ce138 ?! Th=174 Be Mg Ca Zn Sr Cd Ba
Table 17 (M11)	~~CeLaDi!! x45~~ Yt93 Yt^2O^3 CeLaDi!! Ce=138 ~~CeLaDi Zr? 68! Er?? Er^2O^3~~ B Al In Tl Ti=50 Zr=90 ?Ce=138 Th231 C Si ?=72?! Sn Pb
Table 19 (M13)	Ag Cd In Sn Sb Te J Cs Ba La Ce
Table 20 (M14)	Rb Sr ?=90 Yt Zr Nb Mo ?=98 Ag Cd ?=113 In Sn Sb Te J Cs=133 Ba=133 ?=135 La ?138 Ce ?Di=143? — ?Er=?168·9?
Table 21 (L1)	Cr Mo W Ur Mn Ru Fe Rh Ce Pt Co — Ir Ni Pl Os

Fig. VII-2(a).

Table 23 (M16)	Rb Sr (Yt=92) Zr Nb Mo 99 Ru Rh Pl Ag (Ag) Cd In Sn Sb Te J Cs Ba=137 ~~Di~~ La Ce=138 – – – – – – – – – – – – – – – Er Di Ta=182
Table 24 (M17)	Rb Sr 88 Zr Nb Mo 99 Ru Rh Pl Ag Cd In Sn Sb Te J Cs Ba=137 [Di=139?] Ce=138? – – – [Ce? La? Di? Er?] – 163 – – – – – – 191 – – Ta=182
Table 25 (M18) [Table 33 (P10)]	Rb Sr [Yt?=92?] Zr Nb Mo 98 Ru Rh Pl Ag [Ag] Cd In Sn Sb Te J Cs Ba=137 [Di=143?] Ce=138 – – – [La? Di? Er?] – – – – – – – – – – – Ta=182
Table 26 (M19) [Table 30 (P7)] – "Natural system"	Rb Sr [?Yt=88?] Zr Nb Mo 100 Ru Rh Pl Ag [Ag] Cd In Sn Sb Te J Cs Ba=137 –=137 Ce=138? – – – —— – – – – – – – – – – – Ta=182

Fig. VII-2(b).

Remarks associating cerium and its analogues with the iron, palladium and platinum families are to be found also in the two articles on the periodic law which Mendeleev wrote later in 1869, Atomic volumes (R.) and On the quantity of oxygen (R.).[9]

This tendency by Mendeleev at this time to consider cerium and its analogues in a class with the iron, palladium and platinum elements was based primarily upon the recognition of a general similarity of family-type in the sense that within each family the members have atomic-weight values which are very close (unlike the case for the alkali metals, halogens, etc.), rather than upon the recognition of particular chemical analogies between the iron, palladium and platinum elements on the one hand and cerium and its analogues on the other (Mendeleev did, however, note a certain minimal degree of chemical analogy between the cerium family and the iron, palladium and platinum familes - see below). That the grounds for Mendeleev's association of these families were primarily not of a chemical nature is illustrated in the 3rd instalment of the 1st edition of Principles of Chemistry (publ. March 1870), where the chemical properties of the cerite and gadolinite elements are discussed not in conjunction with those of the iron, palladium and platinum elements, but together with those of zinc and cadmium. The chemical analogy of the cerite and gadolinite elements to zinc and cadmium was seen here by Mendeleev not merely in the basicity and assumed divalence of the rare-earth elements, but also, and more specifically, in their ability (like Cd and Zn) to form double sulphates with potassium sulphate.[10] In this same issue of Principles of Chemistry Mendeleev also again drew an analogy between the cerite family and the iron, palladium and platinum families on the basis of the "close-valued (blizkie) atomic weights" of the members within each family.[11] He now went even further than before in his (predominantly) non-chemical association of these families, not only expanding upon the analogy between the atomic-weight relationships within the families (and introducing at the same time a parallel general chemical analogy, concerning oxidation-tendencies within the families), but also pointing to a simple approximate atomic-weight relationship between the families:

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[9] Atomic volumes, p.63 (PLBA, 34); On the quantity of oxygen, p.20, footnote (PLBA, 57).

[10] Pr.Ch., R-1, instalment 3 (March 1870), Ch.V - "Zinc and cadmium (Indium, the cerites and the gadolinites)" - p.190 (PLSM, 289).

[11] PLSM, 293-4.

> Cerium, lanthanum and didymium have close-valued atomic weights, like Fe, Co and Ni; and the atomic weight of Ce (92) is less than for La (94) and Di (95), just as that of Fe is less than for Co and Ni.[12] Also, cerium shows a greater tendency to oxidation than La, which itself shows more tendency than Di - just like the case with Fe, Co and Ni. The atomic weights and compounds of the palladium metals (104-106) and platinum metals (197-199) are insufficiently known and show such similarity within the groups that it is not possible to test the applicability of the above-mentioned relationships to these analogues. We point out the additional fact that the atomic-weight values of the elements of the iron group are a little less than ½ those of the cerite and palladium groups, and the platinum group shows atomic-weight values about twice as great as those of the cerite and palladium groups. We cannot think that such relationships are accidental; by noticing and investigating them we may hope to attain an understanding of the cause of the analogies.[13]

About 6 months after the publication of this passage, in the summer-early autumn of 1870, Mendeleev drew up table 16 (M10), the first of his known periodic tables since table 11 (M8) to include any of the rare-earth elements. In table 16 (M10) he introduced a new atomic-weight value for cerium - Ce = 138, based upon the formula-type R_2O_3 instead of RO for the usual oxide of this element (see Ch. VI, sub-section B-1-c). The places and atomic-weight values assigned by Mendeleev to the various rare-earth elements which were included in his periodic tables from the time of his introduction of "Ce 138" into table 16 (M10) up to the time when he drew up his "natural system" table 26 (M19) are shown in Fig. VII-2 (pp.412-413). During this period Mendeleev came to take the atomic-weight values of Er, La and Di as being in the range 135-180, corresponding to the formula-types R_2O_3 or RO_2 for the usual oxides (see Ch. VI, sub-section B-1-d, for an outline of the atomic-weight changes made by Mendeleev for yttrium, erbium, lanthanum and didymium between March 1869 and early 1871). It is seen from Fig. VII-2 that in the tables 21 (L1), 24 (M17) and 25 (M18) Mendeleev again showed signs of a tendency to classify certain rare-earth elements with the elements of the iron, palladium and platinum families. However, whereas previously he had associated only the cerite elements with these latter families, he now came to include also erbium (a gadolinite element) in this association. In table 21 (L1) only Ce is placed between the palladium and platinum elements; but in each of the tables 24 (M17) and 25 (M18) Mendeleev (tentatively) placed a group of rare-earth elements including Er between the palladium and platinum

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[12] Mendeleev here appears to be drawing attention to the fact that the atomic-weight difference Di - La is less than the difference La - Ce, just as the difference Ni - Co is less than the difference Co - Fe.

[13] Colls., 14, 301; Sc.Ar., 806.

families in group VIII. Mendeleev's placing of rare-earth elements in the group-VIII region of tables 21 (L1), 24 (M17) and 25 (M18) was undoubtedly encouraged by the fact that the new atomic-weight values which he had assumed for these elements showed a reasonably close correspondence to the values of ca. 150 demanded for the missing family of elements whose existence between the palladium and platinum families in group VIII was suggested by the symmetry of his recently-extended periodic table. However, the lack of any significant chemical basis for such a classification of rare-earth elements resulted in the clearly low degree of conviction with which Mendeleev made his proposals in this direction.

Table 33 (P10) (March 1871), the published counterpart of table 25 (M18), was the only published periodic table of Mendeleev's to contain rare-earth elements in the group-VIII region, this placing being extremely tentative. After the publication of table 33 (P10) no further proposals for including rare-earth elements in group VIII were made by Mendeleev. In his article The periodic lawfulness of the chemical elements (G.; publ. Nov. 1871) he had the following to say against placing cerium, lanthanum and didymium in the unoccupied places which were marked in group VIII between the palladium and platinum families in table 36 (P12):

> ... the known properties of these elements [sc. cerium, lanthanum and didymium] do not correspond to the properties of the missing members of group VIII. Thus, the cerite metals are reduced with difficulty, and give few forms of oxidation; they have the properties of fairly distinct bases in their usual oxides, and do not, as far as is known, give characteristic ammines and cyano-complexes like the metals of group VIII - in short, they are not analogues of the group-VIII elements. And there is yet more proof. The specific gravity of cerium according to Wöhler is 5.5. If its usual oxide is taken to be CeO, then Ce = 92, and the atomic volume = 17; if we assume the oxide to be Ce_2O_3, then Ce = 138 and the atomic volume = 25. Neither of these volumes corresponds to a member of group VIII, where we find elements of much smaller atomic volume.[14]

By the time of his construction of table 26 (M19), December 1870, Mendeleev had already come to place cerium fairly firmly in that position in the periodic table which it was to retain in all of his subsequent tables, viz. in group IV (as an analogue of Zr) in the Cs - Ba row of the short-form table.[15] The placing which was suggested (correctly) for yttrium in table 26

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[14] Op.cit., pp.185-6 (PLBA, 142). A little earlier in the same article Mendeleev had written: "The three elements contained in cerite - cerium, lanthanum and didymium - show both close-valued equivalents (ca. 45) and many similarities ... The thought involuntarily arises that here we have elements like the iron group, especially as cerium shows many particular similarities to manganese. But this idea must be rejected upon closer acquaintance with the cerite metals" (ibid., pp. 184-5; PLBA, 141). Just what Mendeleev has in mind here when he talks of the "many particular similarities" between cerium and manganese is not at all clear; he does not give any examples in this article, nor does he appear to do so elsewhere.

[15] See Ch. VI, sub-section B-1-c.

was also retained by Mendeleev, although initially with a considerable degree of uncertainty.[16] In contrast to the cases of cerium and yttrium, Mendeleev's attempts to fit La, Di and Er into the periodic system were far from final by the time he drew up table 26; in fact, not one of these elements was included in table 26 itself. In general, Mendeleev's attempts to place lanthanides other than cerium in the periodic system after the time of his compilation of table 26 encountered difficulties in two directions: first, there was the uncertainty and change which throughout his life tended to characterise the state of knowledge of the lanthanide elements; and secondly, although the symmetry of his periodic table indicated that an appreciable number of as yet unfilled places existed in the region of the table between Ba and Ta (see Ch. VI, sub-section C-2-d), and although the atomic weights of known rare-earth elements appeared to place these elements into this very region of the table, the properties found for these rare-earth elements did not in general coincide with those to be expected (on the basis of interpolation of the pattern of periodicity shown by the lighter and heavier elements into the atomic-weight region between Ba and Ta) for the missing elements which were indicated for this region.

The published version of table 25 (M18), viz. table 33 (P10), appeared in the article On the place of cerium (G.; publ. March 1871); and the published version of table 26 (M19), viz. table 30 (P7), appeared in the article A natural system of the elements (R.; publ. Feb. 1871). On the question of placing "cerium and its satellites" in the periodic system Mendeleev wrote in On the place of cerium, "As far as the latter [sc. the 'satellites' or analogues of cerium, as opposed to cerium itself] are concerned, while their compounds and atomic weights are not known with any conviction it is difficult to give them their proper places; but cerium itself, and its compounds, have already been investigated so thoroughly that in this case we may speak with confidence".[17] Later in the same article he wrote:

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[16] This initial uncertainty regarding the placing of yttrium is clearly indicated in Mendeleev's use of the term "dvi-boron" in his articles A natural system of the elements (R.; publ. 1871) and The periodic lawfulness of the chemical elements (G.; publ. 1871) (see Ch.VI, pp.382 - 3). It is apparent in a manuscript of late 1871 in which Mendeleev discusses the atomic weight of yttrium (see PLBA, 182-3); and is to be seen also in the fact that Mendeleev included yttrium as a queried entry in his periodic tables before 1873 (i.e. before table 38).

[17] PLBA, 60 and 62. Although Mendeleev here says that "we may speak with confidence" as regards the placing of cerium, he did in fact express a slight lingering doubt about this placing 8 months later (see Ch. VI, p. 341).

> I present in conclusion a table [sc. table 33 (P10)] which expresses the system of all the elements in full accordance with the periodic lawfulness. Only yttrium*, erbium, didymium and lanthanum are not placed in it,[18] because their properties and atomic weights seem to me to be still insufficiently firmly established ...

> *If we take for yttrium the equivalent obtained by Bunsen (61.7) and change the formula of its oxide to R_2O_3, then Yt = 92.5 can be placed at III-4 ...[19]

In the text of the original Russian manuscript version of this article the following footnote was appended to the word "erbium" in the above passage:

> Changing the atomic weight of erbium in the same way as for yttrium [sc. assuming the formula Er_2O_3 for the oxide of erbium], Er = 169 perhaps occupies the place III-8 [sc. in table 25 (M18)], in which case its atomic weight ought to be about 190.[20] Changing the atomic weights of lanthanum and didymium in the same way, we obtain La = 140.4; this corresponds perhaps to V-6.[21]

A similar picture of uncertainty concerning the placing of the rare-earth elements other than cerium in the periodic system is presented in Mendeleev's article A natural system of the elements, which was written less than a month after On the place of cerium in late 1870; there are, however, certain differences between the two articles as regards the specific conjectures which are made concerning the placing of these elements. In A natural system of the elements Mendeleev discussed in some detail the properties to be expected for the elements occupying the places III-4 ("dvi-boron") and III-6 in table 30 (P8), without committing himself to any final identification of these elements with particular known (but poorly characterised) rare-earth elements (see Ch. VI, pp. 382 and 393). He acknowledged, however, that "dvi-boron" is "very probably" yttrium;[22] and that the properties of lanthanum and didymium "permit us to think" that one of these elements belongs to the place III-6.[23] He suggested, on the basis of a consideration of the stoichiometry of its hydrated double sulphate with

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[18] Contrary to what he says here, Mendeleev does in fact include yttrium, erbium, didymium and lanthanum in table 33 (P10), albeit extremely tentatively with the entries not only accompanied by question-marks but also enclosed in parentheses.

[19] PLBA, 65.

[20] This value of 190 given for the atomic weight of the element occupying the place III-8 in table 25 (M18) is clearly a mistake (Ta, in V-8, has an atomic weight of 182); it is probably meant to be 180.

[21] See PLBA, 694.

[22] Op.cit., p.48 (PLBA, 93).

[23] Ibid., p.49 (PLBA, 94).

potassium, that didymium (as Di = 144, corresponding to the oxide-formula Di_2O_3) "more probably" than lanthanum occupies III-6 in table 30, lanthanum (as La = 180, corresponding to the oxide-formula LaO_2) occupying instead the place IV-8. In this article Mendeleev made no suggestion about which particular place might be occupied by erbium. Towards the end of A natural system of the elements Mendeleev made a general remark to the effect that perhaps "certain cerite metals" occupy places between Ce and Ta in the periodic table.[24]

Mendeleev's attempts at including the lanthanide elements in his periodic tables after 1870 are indicated below in Fig. VII -3 (standardised to the vertical short-form arrangement). With the exception of tables 30 and 33, which are represented in Fig. VII-2, all of the periodic tables published by Mendeleev after 1870 are represented in Fig. VII-3. To the entry "$(?^2)$" in table 45 (P20) (1880) is appended the footnote: "Possibly didymium (Di = 146) occupies this place, if its oxide corresponds to the formula DiO_2, and its peroxide to Di_2O_5". A footnote to the entry "Ce = 140" in table 57 (P30) (1902), and a corresponding footnote to table 63 (P36) (1906), will be considered later.

We see from Fig. VII-3 that apart from Ce, the lanthanide elements which Mendeleev included in his published periodic tables drawn up after 1870 and before 1881 were La, Di and Er, although in one of these tables - viz. table 42 (P17) (1877) - he omits Di. In all of Mendeleev's tables of this period up to 1881 Er was included two places before Ta, i.e. in the place III-10[25], in accordance with the formula Er_2O_3 for its (only, and hence highest) oxide, and with an assumed atomic-weight value of 178 or 175[26]. This value 178 or 175 for the atomic weight of Er differs appreciably from the value of ca. 168 which was indicated at the time for this element (taking it to be trivalent) on the basis of the experimentally-determined

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[24] See Ch.VI, n.209 and the quoted passage to which it refers.

[25] This designation "III-10" is in terms of Mendeleev's complete system of numeration of the series of the short-form periodic table, adopted first in table 36 (P12) (Nov. 1871). The same place in table 31 (P8) (Feb. 1871) was in fact still designated "III-8", in accordance with Mendeleev's earlier (incomplete) system of numeration of the series.

All subsequent references in the present chapter to places in Mendeleev's periodic table will be in terms of his later (complete) system of numeration of the series.

[26] Although in table 39 (P15) (1875) erbium is given an atomic weight of 178, in the text of the article in which this table is found Mendeleev lists erbium with an atomic weight of 171 (Remarques à propos de la découverte du Gallium, Compt. Rend., 81, p.970; PLBA, 200). He does not comment upon this discrepancy.

	II	III	IV	V
Table 31 (P8) (Feb. 1871)	Ba = 137	?~~138~~=La?=Di? (144) ?La^2O^3. LaX^3?	Ce=140 (138?) $CeCl^3$ Ce^2O^3 CeO^2 CeX^3 CeX^4 CeK^2X^6	~~142~~
	~~158~~	~~160~~	~~162~~	~~164~~
	~~177~~	?~~178~~=Er? (169) ?Er^2O^3 ErX^3?	?~~180~~=Di?=La (187) ?DiO^2. DiX^4?	Ta=182
Table 32 (P9) (Feb. 1871) [Tables 35 (P11), 36 (P12) (Nov. 1871); 37 (P13) (1872); 38 (P14) (1873)]	Ba	Di?	Ce	—
	—	—	—	—
	—	Er?	La?	Ta
Table 39 (P15) (1875)	Ba 137	?Di 138	Ce 140	»
	»	»	»	»
	»	Er 178	?La 180	Ta 182
Table 41 (P16) (1877)	Ba 137	La? 138	Ce 139	Di? 142?
	—	—	—	—
	—	Er 175	? 180	Ta 182

Fig. VII-3(a).

	II	III	IV	V
Table 42 (P17) (1877)	Ba	La	Ce	—
	—	—	—	—
	—	Er	?	Ta
Table 43 (P18) (1877) [Table 44 (P19) (1879)]	Ba	La	Ce	?
	—	—	—	—
	—	Er	Di?	Ta
Table 45 (P20) (1880)	Ba	?Di (139?)	Ce (141)	($?^2$)
	—	—	—	—
	—	Er (175?)	?La (180?)	Ta
Table 46 (P21) (1881) [Tables 47 (P22) (1881); 48 (P23) (1882)]	Ba .	La .	Ce .	Di .
	. —	. —	. —	. —
	— .	Yb .	— .	Ta .

Fig. VII-3(b).

	II	III	IV	V
Table 51 (P24) (1889)	Ba .	La .	Ce .	Di? .
	. —	. —	. —	. —
	— .	Yb .	— .	Ta .
Table 52 (P25) (1889)	Ba 137	La 138	Ce 140	— —
	— —	— —	— —	— —
	— —	Yb 173	— —	Ta 182
Table 53 (P26) (1889) [Tables 54 (P27), 55 (P28) (1895); 56 (P29) (1898)]	Ba	La	Ce	Di?
	—	—	—	—
	—	Yb	—	Ta
Table 57 (P30) (1902) [Tables 58 (P31) (1902) to 65 (P38) (1906)]	Ba = 137·4	La = 139	Ce = 140	—
	—	—	—	—
	—	Yb = 173	—	Ta = 183

Fig. VII-3(c).

equivalent weight of ca. 56. Mendeleev took the atomic weight of Er as 175-8 at this time because this was the value required on the assumption of regular atomic-weight increase in his periodic table for the element occupying the position III-10, and the chemical properties of erbium and the stoichiometry of its compounds had led him to feel that it was here that erbium belongs. He considered the discrepancy between the value Er = 175-8 and the empirically-indicated value of ca. 168 to arise from an error in the experimental determination of the equivalent;[27] in fact, however, it was Mendeleev's value which turned out to be wrong, the atomic weight of erbium actually being ca. 166 (H=1). The places assigned by Mendeleev to lanthanum and didymium in his published tables drawn up after 1870 and before 1881 were, unlike the case of erbium, not constant: these two elements alternated between the positions III-8 and IV-10 during this period; and in a footnote to table 45 (P20) (1880) came the additional suggestion that perhaps didymium occupies V-8. Whichever of these elements was placed by Mendeleev at any given time in the position III-8 was taken to be trivalent with an atomic-weight value of ca. 138; the element at IV-10 was taken to be tetravalent with an atomic weight of ca. 180.

We note here in passing that table 45 (P20) (1880) was the first of Mendeleev's published periodic tables to include the rare-earth element scandium, the discovery of which in 1879 had strikingly confirmed his predictions for "eka-boron".

In the history of Mendeleev's consideration of the problem of the rare-earth elements after 1880, a very important part was played by his contacts with the Czech chemist Bohuslav Brauner (1855-1935).[28] The first direct contact between the two chemists was a letter (in German) dated 17th January 1881 from Brauner to Mendeleev; accompanying the letter were off-prints of two articles by Brauner - On the atomic weight of beryllium (E., G.; 1881) and On the specific volumes of oxides (E., G.; 1881, written jointly with Watts).[29] The contents of this first letter from Brauner to Mendeleev are known only sketchily, from Mendeleev's reply (in German) of 27th January (O.S.)/8th February (N.S.) 1881, and from a reference to the letter in a subsequent communication from Brauner to Mendeleev, 9th March 1882 - "As you see from my detailed letter of 17th January 1881, at first

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[27] See, for example, The periodic lawfulness of the chemical elements (G.; 1871), p.194 (PLBA, 148).

[28] Mendeleev's scientific contacts with Brauner are discussed in Bibl. 38, Brauner - associate of Mendeleev (R.)

[29] See Bibl. 38, pp. 14, 117-8. At the time of writing this first letter to Mendeleev, Brauner was in Manchester.

I was of the opinion that didymium - either wholly or in part - may be the element at VII - 6 (Em = 100)".[30] On 17th February 1881 Brauner wrote a second letter to Mendeleev, comprising 32 closely-written pages in German. Among the topics discussed by Brauner in this letter were the periodic law and the placing of the rare-earth elements - particularly didymium - in the periodic system. He wrote:

> I began to study the periodic law only in 1877, before that knowing absolutely nothing about it. I learned about it first from "Modernen Theorien" [sc. Lothar Meyer's Die modernen Theorien der Chemie, 3rd edn., 1877, which refers to Mendeleev's article in Annalen, 1871], and then went on to read your article [sc. The periodic lawfulness of the chemical elements (G.), Annalen, 1871] in the original ... I carried your article with me everywhere, and there was no greater pleasure for me than to study it and ponder over its various aspects while lying in solitude on the soft moss in the forest ... What particularly absorbed my attention was the section on "The application of the periodic law to the determination of the atomic weights of the little known elements" and the communication on changing the atomic weights of the rare earths, and I attempted to link with the periodic system the new facts which had been discovered in this field since 1871.[31]

Continuing in this letter, Brauner indicated that already in 1877 he had felt that didymium should be placed (as Di = 147) in position V-8 of the periodic table, in accordance with the assumed formula Di_2O_5 for its highest oxide. He acknowledged that at first "there were no analytical proofs and numbers" upon which to base such an assumption, but claimed that after certain initial failures he had in 1880 eventually produced an impure sample of Di_2O_5.[32] Further experiments in 1880 to obtain pure Di_2O_5 led him, he recounted, to think that "didymium is a mixture of two bodies, of which one, although colourless, is not lanthanum"[33] - a conclusion borne out five years later by Auer von Welsbach's separation of didymium into neodymium and praseodymium.

Later in the same letter of 17th February 1881 Brauner discussed also the placing of Ce and La in the periodic table. He reported his success in obtaining the double salt $3KF.2CeF_4.2H_2O$, concluding from this that "the tetravalence of cerium (the formation of CeX_4) has been completely and finally proved, and its placing in the system established as Ce = 141 at IV-8".[34] On the basis of "thorough researches" - by which he seems to be referring to quantitative analyses of compounds, and the determination of the specific heat

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[30] Ibid., p.17. The symbol "Em" stands for "eka-manganese".

[31] Ibid., pp. 23-5.

[32] Ibid., p.25.

[33] Ibid., p.32.

[34] Ibid., pp. 34-5.

of the metal - Brauner concluded that "lanthanum is not $La^{IV} = 180$, but $La^{III} = 138$", placing this element in position III-8 in the table.[35] On the question of the other rare-earth elements Brauner in this letter made the following somewhat conservative remarks, which sound almost like a proscription of discovery of further rare-earth elements:

> Do you not think, however, that it is better to study thoroughly an old element, than by the discovery of a new element bring confusion into this field of chemical asteroids?[36] Ytterbium and scandium (terbium?) have already found their places, but mosandrium, philippium, decipium, samarium, X, holmium and thulium - which for the time being are enough for us - and also Y_α and Y_β (Marignac), are not yet accommodated![37]

Brauner is known to have sent Mendeleev a further three letters in 1881 - on 8th June, 4th July and 21st October. In the July letter he reported that he had at last obtained pure Di_2O_5, analysis of which had given the atomic-weight value Di = 146.58, and the specific gravity of which agreed with the placing of Di in position V-8 in the periodic table. Also in this letter he wrote, "believe me, you will scarcely find anyone on this earth who has more enthusiasm than I for the periodic law".[38]

Brauner's results on didymium were communicated by Mendeleev to a meeting of the chemical section of the Russian Physico-Chemical Society on 8th (O.S.)/20th (N.S.) October 1881. In the report of this meeting Mendeleev is recorded as having said:

> The placing of didymium in group V, as could be conjectured earlier by considering its oxide [sc. usual oxide] to be Di_2O_3 and its highest state of oxidation to be Di_2O_5, has now been confirmed by Brauner in a new series of as yet unpublished researches which he has reported to me by letter ... Thus, those of the metals of this group [sc. the group of cerites and gadolinites] which have been best investigated already find definite places in the periodic system ...[39]

Later in this report - accompanying which was Mendeleev's table 46 (P21) - we find the following remarks:

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[35] Ibid., p.35.

[36] Brauner's reference here to the rare-earth elements as "chemical asteroids" can be seen as a foreshadowing of his "asteroid" hypothesis of 1901 regarding the placing of the rare-earth elements in the periodic table (see later).

[37] Bibl. 38, pp. 35-6. The substances "mosandrium" (Smith), "philippium" (Delafontaine) and "decipium" (Delafontaine) turned out to be mixtures of various rare-earth elements; "X" (Marignac, Soret) was later shown to be holmium; "Y_α" was gadolinium, "Y_β" samarium.

[38] Ibid., pp. 38-9.

[39] J.Russ.Phys.-Chem.Soc., 13 (1881) no. 3, section 1, p.518 (PLBA, 204).

Mendeleev further pointed out that by arranging the elements in a periodic system of the form presented here, it becomes evident that all of the cerites and gadolinites which have been well investigated stand together, side by side with their satellites, the colourless ones (Sc, Y, La, Yb, Th) occupying the free places of groups III and IV; and for the insufficiently investigated ones there remain enough free places next to elements which give many coloured compounds. Thus, between Ce and Th there should be an element the highest oxide of which will have an equivalent of ca. 105, the lowest oxide an equivalent of ca. 135; after Mn should follow eka-manganese with an atomic weight of ca. 100 ... Mendeleev's confidence that the periodic law will be applicable to the cerite and gadolinite metals is based upon the following: first, the fact that the changes in the atomic weights of Ce, Y, etc. (from RO to R_2O_3) suggested by him in 1870 on the basis of the periodic law have been confirmed by many new observations and researches, and have been accepted first by Clève and subsequently by everyone else; and secondly, the fact that ... Mendeleev in 1871 predicted the properties of eka-boron, now completely confirmed in the work of Clève and Nilson on scandium ..., and this would not have happened if the periodic system were not able to embrace the properties of the cerites and gadolinites, and provide a true understanding of them.[40]

A little later, in early 1882, was published part II of the 4th edition of Principles of Chemistry (R.), where the problem of placing the rare-earth elements in the periodic table was discussed by Mendeleev at some length:

... to cerium we should assign the atomic weight ... 141. With this atomic weight cerium ... stands in group IV in series 8, following after Cs = 133 ..., Ba = 137 ..., and lanthanum La = 138, if we take the compounds of the last element to be LaX_3 ... This atomic-weight value for cerium, indicated by the composition of its two oxides and by the periodic system, was shown to be justified by the determination of its specific heat, made by me in 1870 and later by Hillebrand. Hillebrand obtained, moreover, by galvanic decomposition of salts, metallic lanthanum and didymium, and found that their specific heats are close to that of cerium, approximately 0.04; and therefore we are justified in giving them atomic-weight values close to that of cerium ... When La, Ce, Di had found their place in the system of the elements, when they had been shown to be among the elements of the even rows, it was to be expected that there would be elements similar to them to be found also in the even rows, in the neighbourhood of Ce, La and Di - just as in the odd (uneven) rows Ga and In are found near the elements Zn and Cd with which they occur in nature, and as the platinum-family metals Ru, Rh, Pd, Os, Ir and Pt, which accompany each other in nature, stand together side by side in the periodic system of the elements. And this expectation is realised in those of the gadolinite metals which have been well studied ... In 1878 Marignac, while investigating the oxide of erbium, ... discovered a new oxide, which he called the oxide of ytterbium Yb ... For ... ytterbium there is, in the system of elements, a place which hitherto could be assigned to erbium, in group III, i.e. taking the atomic weight of Yb as $3 \times \frac{1}{2} (131.3 - 16) = 173$. Thus, all of the well-investigated gadolinite metals - Sc, Y and Yb - have found places in the periodic system near those of the cerite metals, which resemble them in many respects. There remain those elements, such as erbium ..., terbium ..., perhaps philippium, decipium, thulium (Clève), etc., which, certainly, are as yet not known in anything like

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[40] Ibid, pp. 519-20 (PLBA, 205, 207).

a pure state, and which after purification and the determination of their capacity for oxidation and the values of their equivalents, will find places in the even rows close to the places occupied by those gadolinite and cerite metals which have already been well studied. Even the place of didymium, as also its purification, cannot yet be considered as having been conclusively established. It seems probable to me that many of the gadolinite and cerite metals, especially those which are not readily amenable to investigation and separation, undergo oxidation, just as for cerium there exist Ce_2O_3 and Ce_2O_4, and for didymium there probably exist in addition to the usual form of oxide Di_2O_3 also DiO_2 and Di_2O_5,[41] the last of these probably having weak acidic properties. At present the greatest interest is concentrated in improving our inadequate knowledge of such cerite metals as Di, Er, Tb,[42] which give absorption spectra and coloured oxides and salts, and particularly in studying their highest forms of oxidation. We may suppose that some of these elements occupy certain of the remaining free places in the periodic system, for example VI-8 and VII, following after didymium, with atomic weights of about 146. They may, like Cr and Mn, give lower oxides which are basic and higher oxides which are acidic, all of these oxides being coloured. In group VII, in series 6, there is a missing analogue of manganese, the atomic weight of which will be ca. 100. If analogues of manganese turn out to be found among the coloured gadolinites and cerites they will, in their higher degrees of oxidation RO_2, RO_3, R_2O_7, have weak basic properties and oxidising tendencies.[43]

From Mendeleev's remarks in his communication on the rare-earth elements to the Russian Physico-Chemical Society in October 1881, from the above-quoted comments from the 4th edition of his Principles of Chemistry, and from the periodic tables 46, 47 and 48 which accompanied these publications, the following observations can be made:-

i) Cerium, as always in Mendeleev's tables after 1870, retained its position at IV-8 in his tables of 1881-2.

ii) In 1881 Mendeleev came to place Di with a fairly high degree of conviction in position V-8 of the periodic table, the place which he had already suggested as a possibility for Di in a footnote to table 45 (P20) in 1880. Mendeleev's placing of Di at V-8 in 1881 seems to have been strongly

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[41] Mendeleev here appends a footnote expressing the view that it would be of great benefit for the understanding of the rare-earth elements to study the lower oxidation states of Nb and Ta, since these latter elements are "evidently intimately associated with the cerite and gadolinite metals both in nature and in their place in the periodic table". In the same footnote he also suggests that it would be similarly beneficial to obtain, if possible, lower oxidation states of Th and Zr, and to study the basic salts ROX_2 of these elements.

[42] Mendeleev is here either using the term "cerite" loosely to include also "gadolinite", or else he has unintentionally omitted to refer to "gadolinite metals" as well as "cerite metals", since Er and Tb are in fact gadolinites, not cerites.

[43] Pr.Ch., R-4, part II (1882) 754-6 (PLSM, 377-80).

influenced by Brauner's private communications to him earlier in the year on the matter of didymium.

iii) In 1881-2 Mendeleev placed La at III-8 (as did Brauner in his letter to Mendeleev of 17th February 1881), in contrast to the placing at IV-10 which he had suggested for this element in table 45 (P20) (1880). Experimental evidence (notably the specific-heat values for the metals) indicated that the atomic weights of both La and Di were close to 140; and since didymium was now taken by Mendeleev to belong to the position V-8, lanthanum fitted naturally into III-8.

iv) Whereas in all of the published periodic tables constructed by Mendeleev during the period 1871-1880 erbium was included in position III-10, in 1881 Mendeleev gave this place to Yb = 173 (ytterbium had been discovered by Marignac in 1878). Er was now dropped from the table, joining the ranks of those rare-earth elements whose properties were considered by Mendeleev to be known with insufficient accuracy and certainty for a judgment to be made about their particular places in the periodic table.

v) In his comments of 1881-2 Mendeleev suggests that the unknown element "eka-manganese" (at VII-6, with an atomic weight of ca. 100 - corresponding in fact to technetium) might turn out to be a cerite or gadolinite element. Possibly Mendeleev was here influenced by Brauner's earlier idea that perhaps "eka-manganese" is actually didymium (see above, p. 424).

vi) Mendeleev's remarks of 1881-2 show a non-committal caution as regards the particular placing - and, in certain cases, even as regards the existence - of the rare-earth elements other than Sc, Y, La, Ce, Di and Yb. However, Mendeleev at the same time firmly believed that despite the uncertainties associated with many of the rare-earth elements, all those which turn out to be genuine elements will, when properly characterised, be found to comply with the periodic law and have an appropriate place in the periodic system.

As can be seen from Fig. VII-3, all of the periodic tables published by Mendeleev after 1882 contained La, Ce and Yb in the same positions as in tables 46, 47 and 48 of 1881-2, viz. at III-8, IV-8 and III-10 respectively. The only other element included between Ba and Ta in any of Mendeleev's post-1882 published tables was Di, which is found in all of these tables up to table 56 (P29) (1898) with the exception of table 52 (P25) (1889), always in the same position as in the tables of 1881-2 (viz. V-8) but now accompanied by a question-mark. In Mendeleev's lecture tables of 1886, tables 49 and 50, didymium is included at V-8 without an accompanying question-mark.

In a letter to Mendeleev dated 9th March 1882 Brauner reported that he had failed to obtain any salts corresponding to the oxide Di_2O_5 which he had claimed to have prepared in a pure state in 1881. He now suggested that perhaps Di_2O_5 might actually be a peroxide (like H_2O_2), and not a salt-forming oxide at all, conceding that if this were indeed so then the formula Di_2O_5 could no longer provide grounds for placing Di in group V of the periodic table (Brauner, like Mendeleev, took the indicator of the group-number of an element to be the highest valency shown by the element in a salt-forming oxide as distinct from a peroxide).[44] Three years later, in 1885, didymium was separated by Auer von Welsbach into two constituents which he called "neodymium" and "praseodymium", neither of which showed any tendency to give an oxide of the form R_2O_5 corresponding to the Di_2O_5 which had been claimed by Brauner.[45] Mendeleev had come to learn of von Welsbach's splitting of didymium very soon afterwards, in the same year[46]; that he could still include didymium in his periodic system in 1898, even as a queried entry, is indicative of his general conservatism in dealing with the problem of the rare earths.

The last of Mendeleev's periodic tables to include didymium, table 55 (P29), was given in his article The periodic lawfulness of the chemical elements (R.; 1898). In a footnote in this article Mendeleev listed the elements neodymium, praseodymium, samarium, gadolinium, terbium, erbium and thulium, remarking that these elements "have not been accommodated by me, because of the doubtfulness of the data (for example, for terbium), or because of uncertainty regarding their very existence as separate elements (this particularly concerns the distinction of neodymium from praseodymium, which correspond to the usually-recognised didymium)".[47] Continuing in this footnote Mendeleev wrote:

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[44] Bibl. 38, p.43.

[45] The highest oxidation states known for neodymium and praseodymium up to the present time are Nd (IV) and Pr (IV), and no peroxide or superoxide is known for these elements which could explain Brauner's "Di_2O_5"; the formula-type R_2O_5 claimed by Brauner for this oxide seems to have been a mistake, arising from faulty analysis or the presence of impurity.

[46] If from no other source, Mendeleev heard about von Welsbach's splitting of didymium from Brauner in a letter of 1885 (see Bibl. 38, p.48).

[47] Bibl.11, vol. 23, half-vol. 45, 1898, p.315, footnote (PLBA, 249). Contrary to what Mendeleev suggests here, neodymium and praseodymium appear to have been more generally acknowledged as elements by this time (late 1890's) than was didymium.

> According to their atomic weights these elements, all very rare and extracted with difficulty, come between cerium and ytterbium, which are also rare elements but which have been better studied. Apart from anything else (especially the question of their independence, i.e. the absence of mixtures) the very composition R_2O_3 for their oxides is subject to doubt, because this composition has been established ... only for the following rare elements - Ce, Y, La and Yb; and to extend this deduction to all of the others is premature.[48]

In his letter to Mendeleev of 9th March 1882 Brauner had remarked: "We should in general be prepared for the possibility that the periodic system will have anomalies in the 8th and 9th rows which are not encountered in other rows. Also, it is not likely that following after Cs there will in I-10 be a still more electropositive alkali metal".[49] What Brauner seems to be saying here is that the elements belonging to the region of the periodic table between Ba and Ta may well turn out to present a break in the pattern of group-membership shown elsewhere in the table. His grounds for such a suggestion appear to have been two-fold: first, there was the empirical evidence that for the known elements whose atomic weights indicated that they belong to the region of the table between Ba and Ta, viz. certain rare-earth elements, the only group-characteristics which had been observed with any degree of certainty were those of groups III and IV; and secondly, it seemed to Brauner implausible that there should exist an alkali metal even more electropositive than caesium, which is what would be required (for position I-10) if the pattern of relationships shown by the elements in the other parts of the periodic table were to extend into the region between Ba and Ta. Brauner's idea of an irregularity in the arrangement of the elements between Ba and Ta, expressed in this letter of 1882 in only general terms, came to acquire a specific form in 1901 in his "asteroid" hypothesis concerning the position of the rare-earth elements in the periodic table. This hypothesis - presented by Brauner at the XIth Congress of Russian Scientists and Physicians, St. Petersburg, December 1901 (at which Mendeleev was present) - proposed that the rare-earth elements of greater atomic weight than Ce should all occupy the same place as Ce in the periodic table, IV-8:

> Just as in the solar system an entire group of asteroids occupies a belt in the place where analogy would suggest the presence of only a single planet, so in the periodic system an entire group of rare-earth elements may occupy a single place ... The elements of the rare-earths ... would make up a special inter-periodic group, to some extent analogous to group VIII ... I imagine this group as an extension of the present group IV, beginning at Ce and ending with an element, as yet unknown, with an atomic weight of approximately 180, lying to the

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[48] Ibid.

[49] Bibl.38, p.43.

> left of tantalum ... probably between cerium and tantalum there are no elements other than rare-earth elements.[50]

With this paper Brauner gave a table illustrating his proposal for placing the rare-earth elements in the periodic system, as shown below in Fig. VII-4.[51]

Shortly after the St. Petersburg congress of December 1901 at which Brauner presented the above paper, or perhaps even during the congress itself, Mendeleev asked the Czech chemist if he would contribute a special section on the rare-earth elements for the forthcoming 7th edition of Principles of Chemistry. Brauner agreed, sending Mendeleev the manuscript of his contribution in the autumn of 1902. This was translated (from German into Russian) and edited (with Brauner's permission) by Mendeleev, and published as planned in the 7th edition of Principles of Chemistry in 1903.[52] For the 8th edition of Principles of Chemistry (1906) Brauner in 1905 supplemented his contribution on the rare-earth elements in the light of the advances which had been made in the knowledge of these elements since the autumn of 1902.[53] In both the 7th and 8th editions of Principles of Chemistry Brauner retained his "asteroid" hypothesis of 1901 which placed cerium and the heavier rare-earth elements together in position IV-8 of the periodic table.

Mendeleev's request to Brauner to write the section on rare earths in Principles of Chemistry arose out of his recognition of the latter's experience and expert knowledge in the field of rare-earth chemistry, coupled with the long-standing friendship of the two chemists, but it did not signify any special attachment by Mendeleev to Brauner's "asteroid" hypothesis regarding the placing of the rare-earth elements in the periodic table. On this last matter Mendeleev had the following to say in the 7th and 8th editions of Principles of Chemistry:

> At the Congress of Russian Scientists in 1901 Professor Brauner proposed placing all of the rare metals in a special auxiliary group with Ce, taking their atomic weights as 140-183. I am unable to refute such a conclusion, but I feel that it would be more prudent to leave

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[50] J. Russ. Phys.-Chem. Soc., 34 (1902) no. 2, section 1, pp. 142-53; pp. 150-2 (Bibl.38, pp. 99-100).

[51] This table includes a place for a higher analogue of Cs, in row 10 - contrast Brauner's suggestion of 1882, quoted on p.430, that the existence of a still more electropositive alkali metal than caesium is unlikely.

[52] Elementy redkikh zemel': Pr.Ch., R-7 (1902-3) 519-30.

[53] Pr.Ch., R-8 (1906) 644-56 (see PLBA, 432-3, for extracts).

Groups	I	II	III	IV	V	VI	VII	O-VIII
Row 7	Ag	Cd	In	Sn	Sb	Te	J	Xe
Row 8	Cs 133	Ba 137	La 139	Ce 140				
				Pr 141				
				Nd 144				
				- -				
				Sm 148				
				Eu 151				
				- -				
				Gd 156				
				- -				
				Tb 163				
				Ho 165				
				Er 166				
				- -				
				Tu 171				
				Yb 173				
				R= 180	Ta	W	190	OslrPt(Au)
Row 9	Au	Hg	Tl	Pb	Bi	-	-	-
Row 10	-	Ra?	-	Th	-	U	-	-

Fig. VII-4 (Brauner, 1901-2).

this question open, especially as Yb = 173 (one of the best investigated of the rare metals) corresponds quite well, according to its atomic-weight value, to the position III-10.[54] cf p 397

This comment on Brauner's "asteroid" hypothesis provides the concluding remark of a passage in Principles of Chemistry in which Mendeleev discusses the problem of the rare earths as one of "three subjects which concern the periodic law but which are not yet in agreement with it" (the other two such subjects which he recognises here being the atomic-weight inversions observed in the periodic table for the pairs of elements Co-Ni and Te-I).[55] Earlier in the same passage Mendeleev had first briefly summarised certain aspects of the history of the rare-earth elements since 1870, and had then said:

> A common composition R_2O_3 is ascribed to the (basic) oxides of all of them [sc. the rare-earth elements], on the strength of their analogy with the above-mentioned oxides R_2O_3 of those rare metals [sc. Y, Ce, etc.] which have found their proper places in the periodic system of the elements. For some of the rare metals with the oxide-type R_2O_3 there is no place in group III of the periodic system, although there are two rows of unoccupied places [sc. in the short-form table: more accurately, one row and two half-rows] for elements with atomic weights in the range 140-183, between Ce = 140 and Ta = 183. I have not yet formed any definite opinion on this matter, which I see as one of the most difficult problems facing the periodic law. However, the researches on many of these metals are evidently insufficient for a firm judgment to be given concerning the composition of their oxides, and I therefore consider it premature to make a final decision.[56]

Also in the 7th and 8th editions of Principles of Chemistry Mendeleev acknowledged, in similar footnotes to tables 57 (P30) and 63 (P36) respectively, that between Ce and Ta "the periodic system of the elements shows a break in its form which demands further investigations". The full footnote to table 57 runs as follows:

> Between Ce = 140 and Ta = 183 an entire large period is wanting; but the series of rare elements (the study of which is not complete), for example Pr = 140.5, Nd = 143.6, Gd = 156, Er = 166, Yb = 173, and others, have, according to present-day knowledge, atomic weights which exactly fill this interval, and therefore in the indicated place the periodic system of the elements shows a break in its form which demands further investigations.

The corresponding footnote to table 63 differs only in certain of the details included in the list of rare-earth elements and atomic weights, thus: "... for example Pr = 141, Nd = 144, Sm = 150, Eu = 152, Gd = 157, Tb = 160, Ho = 165, Er = 166, Tu = 171 and Yb = 173, have, according to present-day knowledge, ... etc. ".

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[54] Ibid., p.624 (PLBA, 336). My underlining.

[55] Ibid. (PLBA, 335).

[56] Ibid. (PLBA, 336). My underlining.

This acknowledgment by Mendeleev in the 7th and 8th editions of Principles of Chemistry of a "break in the form" of the periodic system seems to represent a recognition that whereas there exist known elements whose atomic weights fall within the range 140-183, viz. a whole series of rare-earth elements, the properties of these elements do not appear to correspond to those which are expected on the basis of interpolation into this region of the system of the pattern of periodicity shown by the elements lighter than Ce and heavier than Ta. Unlike Brauner, for example, who had acknowledged the possibility of such an irregularity in the periodic system as early as 1882 (see p. 430), Mendeleev had previously never suggested that perhaps there are elements occupying the region between Ce and Ta which do not conform to the pattern of periodicity shown elsewhere in the system. Certainly he had already suggested in 1871 that there may be a break in the periodic system between Ce and Ta, but only in the sense that there may, for some reason to do with the fundamental nature of the chemical elements, be factors which do not allow the formation of elements having atomic weights in this region;[57] before 1902 Mendeleev appeared always to be of the opinion that if elements with atomic weights between those of Ce and Ta do actually exist, then their properties will eventually be shown to correspond to those expected by straightforward interpolation of the periodic system (see, for example, the passage of 1882 quoted on pp.426-7 where he talks of the rare-earth elements fitting not only into groups III and IV, but also into groups V, VI and VII; and his comment of 1898 quoted on p.430 that to assume the oxide-composition R_2O_3 for rare-earth elements other than Y, La, Ce and Yb was "premature").

Mendeleev's remarks in the 7th and 8th editions of Principles of Chemistry concerning Brauner's "asteroid" hypothesis (see pp.431-3) indicate that apart from any other reasons he was reluctant to accept Brauner's grouping of the rare-earth elements Pr - Yb together with Ce in position IV-8 of the periodic table because of the evident trivalence of Yb in its highest saline oxide. (A placing of all lanthanides at III-8, as is done nowadays, would at the time have been unacceptable to both Mendeleev and Brauner, because both were firmly convinced of the correctness of placing Ce at IV-8 in accordance with its tetravalence in CeO_2 and CeF_4; the rare-earth elements of greater atomic weight than cerium could not then be placed with La at III-8, because this would contravene the principle of

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[57] See Ch.VI, p.396. A similar suggestion by Mendeleev, of the possible non-existence of elements in series 9 of the short-form periodic table, is given in Pr.Ch., R-5 (1889), R-6 (1895), R-7 (1902-3) and R-8 (1906) - see Ch.VI, pp.397-8.

atomic-weight ordering in the table). The analogy drawn by Brauner between the multiple-occupancy of places in group VIII and his "inter-periodic" grouping of Ce and the heavier rare-earth elements at IV-8 does not appear to have been remarked upon by Mendeleev, although it is somewhat reminiscent of Mendeleev's own much earlier tendency to associate the rare-earth elements with the iron, palladium and platinum families (see pp. 411 - 6). As grounds for supporting his proposed multiple-occupancy of IV-8 by rare-earth elements the analogy drawn by Brauner with group VIII is of course weak, since group VIII shows a uniform pattern of multiple-occupancy in the different long periods; also, whereas group VIII shows only triple-occupancy of places (or quadruple-occupancy, with the copper-group elements), the place IV-8 would accommodate 16 elements according to Brauner's suggestion (see Fig. VII-4).

C. Mendeleev's views on the inert gases

Before 1894 - the year in which Rayleigh and Ramsay discovered argon - Mendeleev gave no indication of suspecting that there may exist elements which are chemically inert. In connection with this he himself later wrote (1902):

> In 1869, when ... I showed the periodic dependence between the properties of all elements and their ... atomic weights, not only was no element known which was incapable of forming definite compounds, but there was no reason even to suspect the existence of such elements.[58]

> ... until fairly recently all known elements ... entered, directly or indirectly, into mutual combinations ...; to represent a substance as being entirely devoid of the tendency to undergo any sort of chemical change ... would have been much too bold, and without any basis in reality. But then, in 1894, Lord Rayleigh and Professor Ramsay discovered argon ...[59]

But although Mendeleev did not suspect the existence of inert elements before 1894, already in 1869 he had considered the possibility of the existence of certain unknown elements whose places in the series of elements arranged according to increasing atomic weight corresponded to places which later turned out to be occupied by inert gases - viz. the inert gases Ne, Ar and perhaps also He. Thus in March 1869 he had drawn up a manuscript arrangement of elements, table 7 (M7), in which he suggested the existence of two unknown even-valent elements of atomic weights 20 and 36, and perhaps suggested the existence also of a third unknown even-valent element of atomic weight 2.[60] Kedrov (1953) has claimed this as an anticipation by Mendeleev of the existence of Ne, Ar and He:

> It is completely clear that the unknown elements assumed by Mendeleev ... and designated by him $H^2 = 2$, $x = 20$ and $x = 36$, are none other than those future members of the zero group, He = 4, Ne = 20.2 and A = 39.9 ... It may be considered as established that D.I. [Mendeleev], on the basis of an analysis of his system of the elements, foresaw not only those elements which were later realised in Ga, Sc and Ge, but also the elements of the future zero group, 25 to 30 years before their discovery.[61]

Apart from the poor agreement between the atomic-weight values $H^2 = 2$ and He = 4, not to mention the fact that we cannot even be certain that the entry "$H^2 = 2$" in table 7 (M7) was actually intended to represent an unknown element, there are two more important reasons why Kedrov's claim must be

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[58] Attempt at a chemical conception of the world-ether (R.; publ. 1903, 1905): PLBA, 485.

[59] Ibid.: PLBA, 482.

[60] See Ch.VI, p.379.

[61] Kedrov, Sc.Ar., 64.

considered an exaggeration. First, even if we acknowledge zero as being an even number (as Kedrov does, loc.cit.) the fact remains that Mendeleev's concept of valency did not in 1869 include the possibility of "zero-valence", or complete inertness. And secondly, there are no grounds for thinking that the unknown elements $H^2 = 2$, $x = 20$ and $x = 36$ in table 7 (M7) were considered by Mendeleev to be members of a new group in the periodic table, as the inert gases turned out to be. In table 7 (M7) itself there is no indication at all of Mendeleev's opinion concerning the placing of such unknown elements in the periodic table; but remarks he made elsewhere during the period 1869-71 show that he considered the possibility of the existence of elements occupying the known groups between H = 1 and Li = 7 in the table, and of elements occupying a place in group VIII between F = 19 and Na = 23.[62] He does not appear to have made any suggestion at the time about where x = 36 might be placed in the periodic table (much later, in connection with the problem of placing argon in the table in the 1890's, Mendeleev was to discuss the possibility of the occupancy of a place in group VIII between Cl = 35.5 and K = 39).

Before the discovery of terrestrial helium in 1895 Mendeleev tended towards the view that the "helium" spectrum represented not a new substance but some chemical element which was already known on earth, and which produced this unusual spectrum because of the extreme solar conditions. In 1889 he expressed this opinion in a passage criticising the idea that helium is the "primary matter" of the universe (see Ch.II, p.107); and in 1894 he acknowledged that although the helium spectrum "does perhaps reveal a new simple substance", on the other hand "perhaps it will be shown that the helium line belongs to an element which is already known, because spectra change in clarity and in the position of the visible lines with a change in temperature, pressure and combination. Thus, for example, at the very end of the calcium spectrum Lockyer could see only the line 423 at comparatively low temperatures, whilst the lines 397 and 393 appear at a higher temperature, and at still higher temperatures the line 423 becomes quite invisible".[63]

The discovery of argon was announced by Rayleigh and Ramsay on August 13th, 1894, at the British Association meeting at Oxford (the name "argon" had

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[62] See Ch.VI, pp. 380-1.

[63] Pr.Ch., R-6 (1895) 396, n.35 (written 1894); PLSM, 391-2.

not yet been introduced for this new gas; it came into use about 3 months later, after further extensive demonstrations of the chemical inactivity of the gas[64]. Within a month Mendeleev had written a note on the discovery for the 6th edition of his Principles of Chemistry, suggesting that this new gas was perhaps an allotropic modification of ordinary nitrogen, N_3[65]:

> To the number of well-known and long-established constituents of air we must now - thanks to the remarkable investigations made in the summer of 1894 by the Englishmen Lord Rayleigh and Professor Ramsay - include as a constituent up to 1% by volume of a heavy gas (density ca. 19, if H = 1[66]), inactive like nitrogen, and which was discovered thanks to Rayleigh's observations on the density of nitrogen ... This gas ... is shown to have a density about 1½ times greater than nitrogen (is it not a polymer of nitrogen, N_3?). Also, it is now known that this constituent of the air gives a spectrum containing bright blue lines which are observed in the spectrum of nitrogen.[67] Nothing is yet known about the nature of this gas - its properties, composition, chemical reactions, its name - because it has only just been discovered. If new, more detailed information on this subject appears during the printing of this edition of "Principles of Chemistry" (after August 1894), this will be placed at the end of the book, before the index.[68]

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[64] The name "argon" was derived from the Greek ἔργον ("work") with the prefix α ("not").

[65] The suggestion that argon may be N_3 had already been made by Dewar, in a letter to the Times published on 16th August, 1894. Unlike Mendeleev, who accepted the new gas (perhaps N_2) as being a constituent of the atmosphere (see later), Dewar felt that the N_3 had been produced from ordinary N_2 in the course of Rayleigh and Ramsay's experiments (see Dewar, Chem. News, 70, p.87 - Aug. 24th, 1894).

[66] Mendeleev here means that the density is ca. 19, taking the density of hydrogen gas to be 1.

[67] There is apparently a misprint here. Referring to this sentence six months later, in his article Argon, a new constituent of air (R.; Feb.-March, 1895), Mendeleev wrote: "In chapter V, n.16 bis ... it is printed that in the spectrum of argon are 'blue lines which are observed in the spectrum of nitrogen': this is a misprint, omitting 'not', i.e. it should have read - 'blue lines which are not observed in the spectrum of nitrogen', because there is no general identity of blue lines between the argon and nitrogen spectra" (PLBA, 466, n.7. Kamensky's English translation of this later passage, given in Pr.Ch., E-2, 1897, II, 495, n.7, does not clearly present the true meaning of the passage).

[68] Pr.Ch., R-6 (1895) Ch. V, n.16 bis (written 1894); PLSM, 390.

Such "new, more detailed information" was indeed obtained during the remaining months of 1894: Rayleigh and Ramsay carried out diffusion experiments on atmospheric nitrogen ("atmolysis"), they re-measured the density of argon, attempted in vain to induce it to react chemically, measured its solubility in water, and determined the ratio of its specific heats at constant pressure and constant volume ($\frac{Cp}{Cv} = \gamma$) by means of experiments on the velocity of sound in the gas; Crookes and Schuster investigated the spectrum of argon; and K.S. Olszewski, a professor of chemistry at Cracow and an expert on low-temperature research, studied the properties of argon at low temperatures using liquid ethylene and liquid oxygen as cooling agents and with a hydrogen thermometer. The new results were given in a 54-page paper by Rayleigh and Ramsay entitled Argon a new constituent of the atmosphere, presented by Ramsay at a meeting of the Royal Society on 31st January 1895, and in two shorter papers by Crookes and Olszewski respectively, presented at the same meeting by the authors.[69] These papers were published in full in Philosophical Transactions.[70] Abstracted versions appeared in many other journals.[71] Mendeleev's appraisal of the new developments appeared soon afterwards, in two sources:[72]

i) in a 7-page article by him which was included as an appendix to the 6th edition of Principles of Chemistry (as promised in his initial note on argon written in 1894 for this same edition), entitled Argon, a new constituent of air (R.), written mainly in mid-February 1895 but with a few final comments added later, up to 31st March;[73] and,

ii) in a 3-page report on his views on "the relation of argon to the periodic system" as presented by him to a meeting of the chemical section of the Russian Physico-Chemical Society on 14th March 1895.[74]

The main questions with which Mendeleev is seen to be concerned in these two publications are the following (for some of the questions listed here a particular answer to one or more of the other questions is assumed as a starting-point):-

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[69] This meeting was the largest in the history of the Royal Society: at least 800 people attended.

[70] Rayleigh and Ramsay, Phil. Trans., A 186 (1) 187 (1895); Crookes, ibid., 243; Olszewski, ibid., 253.

[71] Chem. News, 71 (1st Feb. 1895) 51; Nature, 51 (7th Feb., 1895) 347; Proc.Roy.Soc., 57 (1895) 265.

[72] Mendeleev's knowledge of the new developments came from the abstract in Proc. Roy. Soc. (see PLBA, 457, 467).

[73] The original Russian version of this article (Argon, novaia sostavnaia chast' vozdukha), published in Pr.Ch.,R-6 (1895) 749-55, is reprinted in PLBA, 457-70. An English translation by Kamensky is given in Pr.Ch., E-2(1897) II, 491-9 (appendix III), entitled Argon, a new constituent of the atmosphere.

[74] J.Russ.Phys.-Chem.Soc., 27 (1895) section 1, pp.69-72 (PLBA,453-6).

1. Is argon actually a constituent of the atmosphere, or was it perhaps somehow produced by Rayleigh and Ramsay in the course of their experiments on atmospheric nitrogen?

2. Is argon a single substance (in the chemical sense) or a mixture of substances?

3. Is argon a new substance, hitherto unknown to chemistry?

4. Is argon a simple substance (free element) or a compound?

5. The closely related questions - What is the atomicity of the argon molecule? What is the atomic weight of argon? What is the position of argon in the periodic system?

In his Argon, a new constituent of air Mendeleev deals with all of the questions listed here, although in this article he does not distinguish very clearly between the different questions, tending instead to consider them all under the general heading of the question of the "independence (samostoiatel'nost')" of argon.[75] The report of Mendeleev's communication of 14th March to the Russian Physico-Chemical Society deals primarily with the questions in 5, considering very briefly also questions 2 and 4: in this report the questions 2, 4 and 5 are clearly distinguished from each other.[76] The overall picture of Mendeleev's views during the period February-March 1895 concerning questions 1-5, compounded from both of the available sources, is as follows, each question being considered in turn in the order listed above:-

1. In Argon, a new constituent of air Mendeleev wrote, "From the data which have been obtained so far, we must conclude with its discoverers that argon belongs among those gases which are permanent constituents of the atmosphere".[77] Recalling his suggestion of 1894 that "argon is perhaps polymerised nitrogen N_3", Mendeleev added, "If this idea were confirmed, still one would not imagine that argon was formed from the atmospheric nitrogen by those reactions by which it was obtained by Rayleigh and Ramsay, but rather that it arises from the nitrogen of the atmosphere under natural conditions".[78]

Apart from the fact of the greater density of atmospheric nitrogen than chemically-derived nitrogen,[79] which had been the original observation by

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[75] See Pr.Ch., R-6 (1895) 752 (PLBA, 461).

[76] See PLBA, 453.

[77] Pr.Ch., R-6 (1895) 749 (PLBA, 458). This conclusion is of course indicated by the very title of Mendeleev's article.

[78] Ibid., n.1 bis (PLBA, 464).

[79] This fact is cited by Mendeleev in his Argon, a new constituent of air, ibid., p.750 (PLBA, 458-9).

Rayleigh which had eventually led to the discovery of argon, Mendeleev saw strong evidence for the presence of argon in the atmosphere also in the results of the "atmolysis" experiments carried out by Rayleigh and Ramsay:

> This hypothesis [sc. "the presence of a heavier gas in admixture with the nitrogen obtained from the atmosphere"] is corroborated by the fact that Rayleigh and Ramsay, having obtained and purified nitrogen (by removal of O_2, CO_2 and H_2O) both from ordinary air and also from air which had undergone atmolysis - i.e. which had been passed along the inside of porous tubes (baked clay pipes ...) surrounded by a rarefied space, part of the lighter gases (primarily nitrogen) thus being removed - found that nitrogen from the air which had undergone atmolysis was heavier than that obtained from air which had not been so treated. This shows that the nitrogen of the atmosphere is mixed with a heavier gas, a gas which leaks through porous walls more slowly than does nitrogen itself.[80]

A further argument in support of the presence of argon in the air was presented by Mendeleev as follows:

> According to the determinations of Rayleigh and Ramsay the solubility of argon in water is approximately 4 volumes in 100 volumes of water at 13°. Consequently argon is almost 2½ times more soluble than nitrogen, and its solubility is close to that of oxygen. Direct experiment proves that the nitrogen obtained from air from boiled water is heavier than nitrogen obtained directly from the atmosphere, which is further indirect confirmation of the presence of argon in the air.[81]

Although Mendeleev's consideration of the available data led him to the conclusion that argon "belongs among those gases which are permanent constituents of the atmosphere", he did nevertheless recognise in the researches of Rayleigh and Ramsay a "weak point" which still allowed some support for the view that the argon obtained by them was, at least in part, produced in the course of their removal of nitrogen as nitrate (by sparking with oxygen and absorption by alkali) or nitride (by reaction with heated magnesium). This "weak point" was seen by Mendeleev in the fact that Rayleigh and Ramsay had not provided any direct experimental corroboration of their explanation (admittedly very plausible in Mendeleev's view) of the isolation in certain of their experiments of very small amounts of argon from chemically-derived nitrogen:

> In these experiments an inert residue of a heavy gas having the properties of argon was observed also when chemically-derived nitrogen was used instead of atmospheric nitrogen, although its quantity was

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[80] Ibid. (PLBA, 459).

[81] Ibid., p.752 (PLBA, 462). The following figures are given by Glasstone, Textbook of Physical Chemistry, 2nd edition, 1960, p.703, for the solubility in water of N_2, O_2 and Ar (in mole fractions x 10^4, at 20°C): N_2, 0.13; O_2, 0.17; Ar, 0.41.

very small. Rayleigh and Ramsay attribute the formation of this residue to the fact that in these experiments the gases were collected with the help of water, and part of the argon dissolved in the water may have passed into the nitrogen. But because the authors of this supposition did not confirm it by any special experiments, this experimental result and its explanation constitute a weak point in their classical researches. With the assumption of the hypothesis that argon is N_3, the obtaining of argon from chemically-derived nitrogen might be explained by a polymerisation of part of the nitrogen in the course of its reacting, although the possibility of Rayleigh and Ramsay's hypothesis, that the argon is evolved from the water employed in the manipulation of the gases, cannot but be acknowledged. From 3,000 volumes of chemically-derived nitrogen, about 3 volumes of argon were obtained; the same amount of atmospheric nitrogen gave about 30 volumes of argon.[82]

2. In the report of Mendeleev's communication of 14th March 1895 to the Russian Physico-Chemical Society we find the following remark: "As regards argon it is necessary to consider ... whether it is a chemical individual or a mixture ... The idea of a mixture is completely unlikely. It is utterly opposed by the observations of Olszewski on the condensation and solidification of argon".[83] Olszewski's researches had shown argon to have a sharply-defined critical temperature, melting-point and boiling-point, indicating chemical purity.[84] In Argon, a new constituent of air Mendeleev made the same point as in the above-quoted passage from his communication of 14th March, but in more specific and somewhat less absolute terms:

> These researches [sc. by Olszewski]... show that argon exhibits a perfect constancy in its properties in the liquid and critical states, which almost [13] disposes of the supposition that it is a mixture of two or more unknown gases ...
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> [13] There remains only the very remote possibility that argon is a mixture of two gases having very nearly the same properties.[85]

In the same article Mendeleev appended to his discussion of the spectrum of argon a footnote in which he says, "Crookes supposed that argon is a mixture of two gases, but since there are no indications of this apart from certain peculiarities of a spectroscopic character, we shall not dwell upon this hypothesis".[86] Crookes had observed that argon shows "two distinct

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[82] Ibid., p.750, n.4 (PLBA, 465). See also PLBA, 456 (from the report of Mendeleev's communication on argon of 14th March, 1895): "The suggestion by Rayleigh and Ramsay that the argon in this case comes from the water is very likely but it is not yet proved".

[83] PLBA, 453.

[84] A table of Olszewski's results is given by Mendeleev in his Argon, a new constituent of air, Pr.Ch., R-6 (1895) 754, n.14 (PLBA, 469).

[85] Ibid., 754 (PLBA, 463, 469).

[86] Pr.Ch., R-6 (1895) 752, n.9 (PLBA, 466).

spectra according to the strength of the induction current employed", one being red and the other "steel-blue"; and he had indeed concluded from this that, "It is not improbable, and I understand that independent observations have already led both the discoverers to the same conclusion, that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum".[87,88] At the same time, however, Crookes acknowledged that in support of the idea

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[87]Crookes, Phil. Trans., 1895 (see n.70, above); these quotations from Crookes' article are given also by Hiebert in Bibl.28, pp. 15-16.

[88]The views of Rayleigh and Ramsay up to this time (Jan. 1895) on the nature of argon appear to have been as follows.

In a letter to Lord Rayleigh dated 24th May, 1894, Ramsay had written, in connection with the discovery of a new constituent of the air with a density greater than that of nitrogen,

"Has it occurred to you that there is room for gaseous elements at the end of the first column of the periodic table? Thus:-

Li	Be	B	C	N	O	F	X	X	X
-	-	-	-	-	-	Cl			
-	-	-	-	-	-	Mn	Fe	Co	Ni
-	-	-	-	-	-	Br			
-	-	-	-	-	-	?	Pd	Ru	Rh

etc.

Such elements should have the density 20 or thereabouts [sc. assuming diatomic molecules, in accordance with the usual pattern for free elements which are gases at normal temperatures, e.g. H_2, O_2, Cl_2], and 0.8 p.c. (= $\frac{1}{120}$th about) of the nitrogen of the air would so raise the density of nitrogen in the ratio 230:231" (see Bibl. 117, p.110).

By August 1894 the density of the new gas had been found to be close to 20, indicating a molecular weight of ca. 40 (later in the year the value of 20 for the density was confirmed in more accurate determinations). The discoverers at this stage believed the gas to be a diatomic form of a new element of atomic weight ca. 20, whose place in the periodic table was probably in group VIII between F and Na, corresponding to one of the X's proposed by Ramsay in his letter of 24th May. This belief was retained until November 1894, when the specific-heat ratio for the new gas was determined as being between 1.64 and 1.66. On the basis of this value for the specific-heat ratio Rayleigh and Ramsay now took argon to be a monoatomic gas, rejecting the idea that the molecule may be diatomic or polyatomic with no rotational or vibrational motion as being "a conclusion improbable in itself and one postulating the sphericity of such complex groups of atoms" (Phil. Trans., 1895; see Bibl. 28, p.14). This posed a new problem as regards the position of argon in the periodic table. If argon be a single element it would have an atomic weight of 40, in which case "there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they may find places in the eighth group, one after chlorine and one after bromine ..." (Phil. Trans., 1895; see Bibl. 28, p.14). The latter suggestion (that argon may be a mixture of two elements of atomic weights of about 37 and 82), rather than Ramsay's earlier suggestion of three X's of atomic weight ca. 20, was presumably the conclusion to which Crookes was referring in the above-quoted passage where he himself suggests on spectroscopic grounds that argon is perhaps a mixture of two or more elements. However, while they had indeed suggested the possibility that argon may be a mixture, Rayleigh and Ramsay nevertheless preferred the hypothesis that it is a single element of atomic

that argon is a single substance was the fact that nitrogen also could be made to exhibit two spectra by varying the pressure and the intensity of the spark.

3. Mendeleev believed argon to be a substance hitherto unknown to chemistry. As reasons for this belief he cited the facts of its distinctive spectrum ("the spectrum of argon ... distinguishes it from other gases"[89]), its unprecedented degree of inertness ("argon has a greater number of negative characteristics, in the sense of having a smaller capacity for reaction, than any other known simple or compound gas"[90]), and its distinctive collection of physical constants (ratio of specific heats = 1.66[91]; boiling-point, melting-point, etc.).

4. In the report of Mendeleev's communication of 14th March 1895 to the Russian Physico-Chemical Society the question is raised as to whether argon is "a simple body or a compound", to which the reply provided is,

> The idea of the complexity of argon seems ... to have low probability. Although the unusual stability observed for argon is shown to a certain degree also by some compounds, nevertheless it speaks much more strongly in favour of acknowledging argon to be a simple body. Also the spectrum of argon is characteristic of a chemically simple individual.[92]

The argument that its exceptional inertness indicates argon to be a simple substance rather than a compound is probably partly intuitive (i.e. if argon were a compound, formed from more than one element by a chemical process, then it would be expected also to be chemically decomposable) and partly based upon the analogy provided by nitrogen, the most inert gas previously known and a simple substance. What Mendeleev has in mind, however, when he says that the spectrum of argon is characteristic of a simple substance rather than a compound is not clear (note that the nature of the spectrum is here cited by Mendeleev as support for the idea that

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weight 40. It is indicative of their confidence in the accuracy of their experimental results that Rayleigh and Ramsay were more ready to accept the possibility that argon is a mixture of <u>two</u> unknown elements, with atomic weights of about 37 and 82, than to accept that it is a <u>single</u> unknown element of atomic weight ca. 37, but whose density they had measured somewhat inaccurately as 20.

[89] <u>Argon, a new constituent of air</u>, <u>Pr.Ch.</u>, R-6 (1895) 752 (<u>PLBA</u>, 461).

[90] <u>Ibid.</u>, p.751 (<u>PLBA</u>, 460-1).

[91] No known substance which was a gas at ordinary temperatures had been found to have such a value for its specific-heat ratio. This value of 1.66 for the specific-heat ratio of argon was not accepted unreservedly by Mendeleev at this time (1895), however (see below).

[92] <u>PLBA</u>, 453.

argon is a simple substance rather than a compound, not for the idea that it has a monoatomic molecule rather than a diatomic or polyatomic molecule); he gives no indication of what he means by this either in his report on argon to the Russian Physico-Chemical Society, or in his article Argon, a new constituent of air (where he describes the argon spectrum at some length).

Also considered by Mendeleev in connection with the question of whether argon is a simple substance or a compound was the value 1.66 obtained by Rayleigh and Ramsay for the ratio of its specific heats (measured by determining the velocity of sound in the gas). According to the theory generally accepted at the time (and still accepted) such a value ($= \frac{5}{3}$) for the specific-heat ratio of a gas indicates that its molecules have translational motion but no rotational or vibrational motion, and consequently that it is a monoatomic gas; for a diatomic or polyatomic gas, having rotational and vibrational degrees of freedom, the specific-heat ratio would be expected to be $\gamma = \frac{5 + x}{3 + x}$, where x is an additional (positive) factor explained to some extent in terms of the principle of equipartition of energy (Maxwell-Boltzmann). The only case known before 1894 where the specific-heat ratio of a gas had been found to be 1.66 was that of mercury vapour, which was indeed monoatomic (as had been shown by vapour-density measurements). Other (diatomic and polyatomic) gases had lower values, as expected, e.g. for CO, H_2 and N_2, 1.4; for Cl_2, 1.33; for CO_2 and N_2O, 1.3.[93] Therefore, according to the current theory, and accepting Rayleigh and Ramsay's value of $\gamma = 1.66$, argon should be a monoatomic gas, in which case it must be a simple substance rather than a compound. While acknowledging this reasoning Mendeleev in 1895 was - primarily from considerations on the placing of argon in the periodic system (see later) - nevertheless reluctant to accept the conclusion that argon is monoatomic; this he was able to do by questioning both the experimental result obtained by Rayleigh and Ramsay, and also the theory which claimed that $\gamma = 1.66$ necessarily indicates a monoatomic gas. Thus, in Argon, a new constituent of air he wrote:

> Because of the significance of the conclusion [sc. that argon is monoatomic]... it is desirable that the velocity of sound in argon be re-determined ... If it should be found that for argon k [sc. the ratio of specific heats] is less than 1.4 ... we could then assume that the molecule of argon contains not one but several atoms ...[94]

But, he added, even if the specific-heat ratio of argon turns out to be confirmed as 1.66, the argon molecule could still contain more than one atom if the specific-heat ratio were to depend upon "chemical energy". This idea is explained in outline both in Argon, a new constituent of air and in

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[93] All of the examples cited here were actually given by Mendeleev himself in Argon, a new constituent of air.

[94] Pr.Ch., R-6 (1895) 753 (PLBA, 462-3, and 467, n.12).

Mendeleev's report on argon to the Russian Physico-Chemical Society in March 1895. In the latter source, for example, we find the following passage:

> We must ... bear in mind that the value of k... varies even between molecules containing the same number of atoms. Thus for the majority of gases containing 2 atoms (nitrogen, oxygen and others) k is approximately 1.4, but for chlorine it is about 1.3. This latter value gives grounds for supposing that the value of k depends not only upon the number of atoms in the molecule, but also upon the chemical energy, the store of inner motion which determines the chemical activity of the body and which for chlorine must be comparatively large. Since for the chemically-active chlorine k is significantly less than 1.4, then perhaps for the extremely inert argon k would be significantly greater than 1.4 even if the argon molecule were to contain 2 or more atoms.[95]

A very similar passage occurs in Argon, a new constituent of air, with the additional remark that "I think these questions might be partially elucidated by determining k for ozone O_3 and sulphur S_6 (at about 500°). In other words I would suggest, though only provisionally, that the value k = 1.66 obtained for argon might prove to agree with the hypothesis that argon is N_3, formed from N_2 with evolution of heat or loss of energy".[96]

Mendeleev's hypothesis of a "chemical-energy" contribution to the specific-heat ratio of a gas is nowhere presented by him in any greater detail than is given in the above-cited passages.

We note that to the extent that Mendeleev was reluctant to accept a specific-heat ratio of 1.66 as indicating a monoatomic molecule for argon (and this reluctance was appreciable) he was also rejecting the relevance of the value $\gamma = 1.66$ for deciding whether argon is a simple substance or a compound.

5. Mendeleev was firmly committed to belief in what he called the "general applicability" (or "generality": obshchnost') of the periodic law - the belief that all elements, including any yet to be discovered, are subject to the periodic law, each having a place in the periodic system.[97] Consequently, once Mendeleev had accepted that argon is a simple substance the question of the atomicity of the argon molecule (or, expressed alternatively, of the atomic weight of the element) was for him necessarily

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[95] PLBA, 454.

[96] Pr.Ch., R-6 (1895) 753, n.10 (PLBA, 467).

[97] A slight weakening of Mendeleev's committment to this idea of the "general applicability" of the periodic law can be recognised in his acknowledgment in the early 20th century of an apparent "break in the form" of the periodic system associated with the placing in the system of the known rare-earth elements of atomic weights in the range 140-183 (see pp. 433-4 in section B of the present chapter).

intimately linked with the question of the place of the element in the periodic system. These questions were considered by him both in Argon, a new constituent of air and in his communication on argon of 14th March, 1895. The discussion of this subject in the report of his communication of 14th March is introduced with the following words:

> Taking argon to be a simple body we now come to consider a series of suppositions about the value of its atomic weight, assuming that the molecular weight of argon is about 40 (but probably a little more than 40, because slight admixture with the lighter nitrogen has been noticed to some extent[98]). The atomic-weight value will clearly depend upon ... the number of atoms contained in the molecule. We shall here examine a series of possible formulae for the argon molecule: A, A_2, A_3 ... A_n.[99]

Mendeleev considered the possibilities for A_n up to n = 6.

a) n = 1, i.e. argon is A = 40.

In his communication on argon of 14th March, 1895, Mendeleev began his consideration of the suggestion that the argon molecule may be monoatomic, corresponding to an element A = 40, with the comment, "In support of this suggestion is the value of about 1.66 found by Rayleigh and Ramsay for the ratio, k, of the specific heats of argon at constant pressure and constant volume, a value considered characteristic of molecules containing a single atom".[100] Having acknowledged this, however, Mendeleev immediately went on to present (as quoted above, on p.446) an outline of his idea that the value k = 1.66 could perhaps also correspond to a diatomic or polyatomic molecule in the case of an extremely unreactive substance like argon; he then introduced his main objections to the assumption of a monoatomic molecule for argon, these being based upon a consideration of the periodic system -

> If we assume that argon contains a single atom in its molecule there is no place for it in the periodic system. If the density of argon is taken to be significantly less than 20 (although this is unlikely, and we would sooner think the opposite[101]), so that its atomic weight comes between those of Cl and K, then argon may be placed in the eighth group of the third series; but the existence of the eighth group in this series is very difficult to admit.

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[98] The nitrogen impurity here referred to by Mendeleev was in fact negligible. His statement that the molecular weight of argon is "probably a little more than 40" was almost certainly motivated less by empirical evidence than by hope: at this time Mendeleev was inclined to believe that argon is N_3 (see later), in which case its molecular weight should be 42.

[99] PLBA, 453-4.

[100] PLBA, 454.

[101] See n.98, above.

> The eighth group is peculiar to the large periods, and establishes a link between the metallic elements of the seventh group of the even series and the similar metallic elements of the first group of the uneven series. Thus, the supposition that the atomic weight of argon is about 40 has low probability.[102]

In other words, Mendeleev felt that if we assume the molecule of argon to be monoatomic, then even allowing (against the indications of experimental evidence) enough scope for error in the determined vapour density of the gas for the atomic weight of the element to fall between those of Cl (35.5) and K (39), the placing of argon in group VIII of the periodic table between these latter elements of groups VII and I would be unsatisfactory on grounds both of chemical analogy and of symmetry of the table. At this stage - quite understandably in view of the many uncertainties associated with the nature of argon, and the absence of any known analogue of the gas - Mendeleev did not think in terms of solving the problem by introducing a completely new group of elements into the periodic table. (The "zero" group in which the inert gases are placed nowadays seems to have been suggested publicly first by Errera in 1900 - see later).

In his Argon, a new constituent of air Mendeleev wrote: "... there is no reason on the basis of existing data for admitting any intermediate element between Cl = 35.5 and K = 39, and beyond potassium all places in the periodic table [sc. in the atomic-weight region of ca. 40] are full ... The hypothesis A = 40 does not admit argon into the periodic system".[103]

b) n = 2, i.e. argon gas is A_2, A = 20.

Mendeleev's willingness in 1895 to doubt the accuracy of the empirically-determined value of 1.66 for the specific-heat ratio of argon and the validity of the theory which restricted such a value to monoatomic gases enabled him without inconsistency still to admit the possibility that argon gas may be diatomic or polyatomic. His consideration in the light of the periodic law of the possibility that argon is a diatomic gas A_2, corresponding to an element A = 20, led him to conclude that this is a much more likely possibility than that of the monoatomicity of argon gas. The only available place in the periodic table at the time for A = 20 was in group VIII between F = 19 and Na = 23. Such a placing of A = 20 might appear prima facie to be open to exactly the same criticisms as would a placing of argon (taking its atomic weight to be somewhere in the range 35.5 - 39) between Cl and K; but although in both cases there would be an inert element in group VIII between two elements of high reactivity and very different character in groups VII and I, providing a sharp deviation from the pattern normally shown in

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[102] PLBA, 454. My underlining.

[103] Pr.Ch., R-6 (1895) 753-4 (PLBA, 463 and 468).

group VIII of a gradual transition between groups VII and I, there were two additional factors which led Mendeleev to consider A = 20 as being more likely. First, such an element would belong to the same row in the short-form table as Li, Be ... F, the so-called (by Mendeleev) "typical" elements whose properties tended to show appreciable deviation from the normal group properties of their heavier analogues; consequently, deviation from the normal character of group VIII could in the case of A = 20 be explained in terms of its position among the "typical" elements, whereas no such explanation is possible for an inert element between Cl and K. Secondly, an element between F and Na in group VIII would not destroy the symmetry of occupancy of this group with respect to the rows of the short-form periodic table (occupancy in alternate rows, viz. in "even" rows), whereas an element between Cl and K in group VIII, occupying an "uneven" ("odd") row, would destroy this symmetry. In the report of Mendeleev's communication on argon of 14th March, 1895, these points are expressed as follows:

> To the second proposal, A_2, corresponds an atomic weight for argon of about 20, and then argon must be placed in the eighth group of the second row of the system, i.e. following fluorine. In this case the same objections can be raised as in the first case [sc. the case of monoatomic argon gas]. Fluorine and sodium provide sharp contrasts. On the other hand, however, there is in this second case the analogy of the existence of the eighth group in the even rows, and if we take into account that the typical row is in many respects peculiar, then a certain possibility presents itself for the supposition that argon has an atomic weight of 20, and this supposition is therefore much more likely than the first (A = 40).[104]

In discussing the possibility A_2 in Argon, a new constituent of air Mendeleev made no explicit use of the symmetry argument which we find in the above passage, although recognition of the fact that group VIII is occupied in only alternate rows of the short-form periodic table is presumably implicit in his comment in this article that "A = 20 ... apparently finds a place in group VIII between F = 19 and Na = 23".[105] He did, however, emphasise in Argon, a new constituent of air the argument based upon the peculiar character of the "typical" elements: "... only the typical character of the elements of small atomic weights can justify placing argon as A = 20 in group VIII among the typical elements; then N, O, F, A are a series of gases".[106]

c) n = 3, i.e. argon gas is A_3 (N_3).

The suggestion that argon might be a triatomic gas was taken by Mendeleev

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[104] PLBA, 454-6. My underlining.

[105] Pr.Ch., R-6 (1895) 754, n.12 (PLBA, 468).

[106] Ibid.

to be no more than the suggestion that argon is N_3: "If argon is thought to contain three atoms in its molecule, then the atomic weight will be about 14, i.e. we need to think that in this case argon is condensed nitrogen N_3".[107] There is no room in the periodic table for any element of atomic weight ca. 14 other than nitrogen.

We have seen (p.438) that as early as August-September 1894 Mendeleev had suggested that argon may be N_3. In February 1895, in Argon, a new constituent of air, he acknowledged that although the value 1.66 recently found by Rayleigh and Ramsay for the specific-heat ratio of argon was certainly awkward for the hypothesis that this gas is N_3, neither this nor any other fact provided conclusive refutation of the hypothesis, whereas many properties of argon actually supported it:

> The suggestion that argon may be ... N_3 ... is not completely eliminated by the latest results, although the specific-heat ratio of 1.66 which has been found for argon speaks against it because according to current knowledge such a value is not possible for a triatomic gas ... I ... frequently return to this hypothesis [sc. that argon is N_3] not only because I have not yet come across any facts which conclusively refute it, but also because the chief properties of argon provide a certain degree of support for the hypothesis.[108]

The various factors cited by Mendeleev in Feb.-March 1895 in support of the view that argon is N_3 were as follows:-

i) The observed vapour density of ca. 20 for argon was close to the value 21 required for N_3; and complete removal of the final traces of nitrogen impurity would tend to raise the measured density of argon.[109]

ii) Argon occurs together with nitrogen in nature, both gases being constituents of the atmosphere.[110]

iii) Argon had been isolated, although in comparatively small amounts, in certain experiments by Rayleigh and Ramsay which had used not atmospheric nitrogen but chemically-derived nitrogen (explained by Rayleigh and Ramsay as argon which had been dissolved in the water over which the gases were collected, a plausible explanation which, however, still remained to be empirically tested).[111]

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[107] PLBA, 456. Mendeleev not infrequently uses the expression "condensed (uplotnennyi) nitrogen" in referring to N_3.

[108] Pr.Ch., R-6 (1895) 749, n.1 bis (PLBA, 464).

[109] Ibid., p.753, n.12 (PLBA, 467-8); see also the passage from the report of Mendeleev's communication of 14th March, 1895, quoted earlier on p.447, to which n.98 of the present chapter refers.

[110] Report, 14th March, 1895: PLBA, 456.

[111] Ibid.; see also the passage from Argon, a new constituent of air quoted earlier on pp. 441-2.

iv) Mendeleev wrote that "the possibility of polymerisation for nitrogen is all the more admissible from the consideration that the augmentation of the atoms in its molecule is not at all unlikely; and polymerised nitrogen, judging from many examples, might be inert if the polymerisation is accompanied by the evolution of heat".[112] The meaning of the first part of this sentence is somewhat obscure in the apparent circularity of its argument; but judging from a remark to be found a few lines earlier in the same passage - "argon is perhaps polymerised nitrogen N_3, showing that relationship towards normal nitrogen N_2 which is shown by ozone O_3 towards normal oxygen"[113] - Mendeleev probably has in mind that the likelihood of the existence of trinitrogen N_3 is enhanced by the analogy provided by the existence of ozone O_3. The second part of the above-quoted sentence is presumably making some of its point in a tacit recognition of the fact that ordinary nitrogen, from which inert N_3 would have to be formed by an exothermic process, is itself fairly unreactive. Mendeleev gave no sign of acknowledging the weakness of taking the existence of ozone, a reactive gas which he realised is formed endothermically from O_2, as analogical support for the existence of an inert gas N_3 which he recognised would have to be formed exothermically from N_2.

v) Mendeleev's consideration of Crookes' work on the argon spectrum led him to feel that the spectrum of argon might turn out to provide certain evidence in support of the hypothesis that this gas is N_3. He wrote:

> [7]... there is no general identity of blue lines between the argon and nitrogen spectra. However, we note that for nitrogen fairly bright lines of wavelengths 585, 574, 544, 516, 457, 442, 436 and 426 are known, which occur also in the spectra (red and dark blue) of argon, judging from the data of Crookes (1895). Of course, we cannot assert that the coincidence of lines here is perfect until special comparisons are made in this respect, desirable particularly for the blue-violet part of the spectrum, and especially for the lines 442-436 because these lines are distinguished by their brightness in both the nitrogen and argon spectra. The above-mentioned hypothesis that argon may be polymerised nitrogen N_3, formed from nitrogen N_2 with evolution of heat, may receive some support if after careful comparison it should be shown that even a few of the spectral lines of the two gases coincide.
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> [8] The argon spectrum at first exhibits the nitrogen lines, but after some time under the influence of platinum (also of Al and Mg, but with Mg the hydrogen spectrum appears) the nitrogen spectrum disappears and the pure argon spectrum remains. Whether we here have polymerisation of nitrogen or merely absorption of the gas is not

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[112] Pr.Ch., R-6 (1895) 749, n.1 bis (PLBA, 464).

[113] Ibid.

clear to me, and perhaps the elucidation of this point will be of benefit for the history of argon. It would be desirable, for example, to know whether or not the volume of the argon changes when it is first subjected to the action of the electrical spark.[114]

vi) Having presented in Argon, a new constituent of air a table listing Olszewski's data on argon at low temperatures togehter with the corresponding data on O_2, N_2 and other gases, Mendeleev remarked, "It is clear from a comparison of the data that for argon ... all its characteristic temperatures (tc, t and t_1) [sc. critical temperature, boiling-point at 760 mm., and melting-point] are higher than for nitrogen. This fully corresponds not only to the higher density of argon, but also to the hypothesis that it is N_3".[115] A higher boiling-point, etc., for argon than for nitrogen is indeed what we should expect in view of the fact that its vapour density (and hence molecular weight) is 1.4 times that of nitrogen; but why Olszewski's results should be thought to support the hypothesis that argon is N_3 rather than any other substance of the required molecular weight is unclear. Mendeleev says nothing further on this matter.

vii) In March 1895 Berthelot announced that he had induced a sample of argon (supplied by Ramsay) to enter into combination with benzene vapour under the action of a silent discharge.[116] The composition of the product could not be determined because of the small amount obtained, but it was said by Berthelot to resemble closely in appearance a product which he had earlier obtained from nitrogen and benzene vapour under similar conditions. Mendeleev commented in his Argon, a new constituent of air, "In this observation by the famous French chemist we can to some extent see a confirmation of the idea ... that argon is a polymerised form of nitrogen ... N_3".[117] Later, in the early 20th century, he was to remark in reference to Berthelot's result: "It is not known whether the argon was pure. There has so far been no elucidation of the result".[118]

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[114] Ibid., p.752, nn. 7 and 8 (PLBA, 466). In the report of Mendeleev's communication on argon, 14th March, 1895, one reason for considering that argon may be N_3 is briefly given as the fact that for argon and nitrogen "many bright lines of their spectra are close" (PLBA, 456).

[115] Pr.Ch., R-6 (1895) 754, n.14 (PLBA, 469).

[116] M. Berthelot, Comptes rend., 120 (1895) 235, 581.

[117] Pr.Ch., R-6 (1895) 755, n. ("final note", dated 19th March, O.S., 1895); PLBA, 469-70.

[118] Pr.Ch., R-7 (1902-3) Ch.V, n.61; R-8 (1906) n.165 (PLSM, 548). The explanation of Berthelot's result was subsequently discovered by Travers (see Bibl.117, p.158): the samples of argon which had been sent by Ramsay to Berthelot had been opened in transit by French customs officials, and consequently Berthelot had unwittingly experimented on air rather than argon.

viii) Unlike the other possibilities considered by Mendeleev for the atomicity of argon, the suggestion that argon is N_3 posed no problem from the point of view of the periodic system. Thus, in discussing the question of the placing of argon in the periodic system Mendeleev wrote in 1895, "It seems to me to be simplest to assume that argon is N_3".[119]

In connection with his conjecture that argon is N_3, Mendeleev suggested certain lines of research:

> ... if argon is N_3 formed with the evolution of heat, its conversion into nitrogen N_2 and into nitride compounds (such as boron nitride or titanium nitride) might only take place at very high temperatures.[120]
>
> ... in the course of further researches upon argon it might be worthwhile to subject it to as high a temperature as possible.[121]
>
> It might be possible to verify the supposition that argon is condensed nitrogen by means of the introduction of boron or titanium into an atmosphere of argon with the passing of electric sparks and with intense incandescence.[122]

d) <u>n = 4 or 5, i.e. argon gas is A_4 or A_5, A = 10 or 8.</u>

These possibilities were dismissed outright by Mendeleev because in such cases argon "will have no place in the periodic system".[123]

e) <u>n = 6, i.e. argon gas is A_6, A = 6.5.</u>

In considering this possibility Mendeleev had the following to say in his communication on argon of 14th March, 1895:

> Finally, if we assume that there are six atoms in the argon molecule, and an atomic weight of about 6.5, we must put argon in the first row [sc. the row of the short-form periodic table which contains H, above the Li - F row]. In this case it would probably occupy a place in the fifth group. Thus, <u>if argon is a pure simple substance the most probable assumptions are that it is condensed nitrogen, N_3, or that it has six atoms in the molecule and is placed in the first row of the periodic table.</u>[124]

The suggestion that an element A = 6.5 in the first row of the short-form periodic table would probably occupy group V rather than some other group in the same row was clearly not made on the basis of an assumption of uniform atomic-weight increments for the series of possible elements between H = 1 and Li = 7, since such an assumption would lead to

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[119] <u>Argon, a new constituent of air</u>: <u>Pr.Ch.</u>, R-6 (1895) 754, n.12 (<u>PLBA</u>, 468).

[120] <u>Ibid.</u>, p.753, n.10 (<u>PLBA</u>, 467).

[121] <u>Ibid.</u>, p.749, n.1 bis (<u>PLBA</u>, 464).

[122] Report, 14th March, 1895: <u>PLBA</u>, 456.

[123] <u>Ibid.</u>

[124] <u>Ibid.</u> My underlining.

the expectation of an atomic weight of ca. 4.5 for the element at V-1. Mendeleev was probably here encouraged instead by the inertness of argon to suggest for it that placing in the first row which would make it a lower analogue of nitrogen. This seems particularly likely when it is considered that the place VI-1 not only appears to correspond better than V-1 to the atomic-weight value 6.5, but also would be supported by an analogy between the molecules A_6 and S_6 (the molecule S_6 is explicitly referred to by Mendeleev in his Argon, a new constituent of air - see earlier, p.446). However, even though Mendeleev did not suggest placing A = 6.5 in group VI, it was perhaps the example provided by S_6 which encouraged him to suggest as high an atomicity as 6 for gaseous argon: argon as A_7, A_8 or A_9 would give an atomic-weight value for A which would appear to fit better into V-1 than does A = 6.5, but no gaseous simple substances of such high atomicities were known.[125]

From the preceding consideration of Mendeleev's comments of February-March 1895 on the question of the atomicity of the argon molecule, we can summarise as follows his order of preference at this time regarding the various possibilities which he discussed (">" signifies "preferred to"):

A_3 ($\equiv N_3$) > A_6 > A_2 > A > A_4, A_5.

The decisive criterion which Mendeleev employed in arriving at this order of preference was that of accordance with the periodic law, as is seen particularly in his reluctance to accept the possibility that argon is a monoatomic gas corresponding to an atomic weight for the element of ca. 40. Among those who showed agreement with Mendeleev's claim that a value of 1.66 for the specific-heat ratio of argon did not provide conclusive evidence of its monoatomicity were Armstrong, Brauner and Nasini, all of whom, like Mendeleev himself, adopted this attitude out of reluctance to accept a failure of the periodic law.[126] Brauner inclined towards Mendeleev's view that argon

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[125] The presence of S_8 molecules has subsequently been recognised in gaseous sulphur.

[126] B. Brauner (Prague), Chem. News, 71 (15th Feb.,1895) 79; R. Nasini (Padua), Chem. News, 72 (22nd Nov.,1895) 247; for Henry Armstrong's view see, for example, Nature, 51 (7th Feb., 1895) 347.

Whereas Mendeleev's argument in support of the possibility of $\gamma = 1.66$ for diatomic or polyatomic argon had been expressed in terms of the vague concept of "chemical energy" as a form of "inner motion" of the molecule (see earlier, p.446), with no apparent regard for the usual theoretical significance which γ had in terms of the translational, rotational and vibrational degrees of freedom of the molecule, the others who accepted the possibility of $\gamma = 1.66$ for di- or triatomic argon tended to do so within the framework of the usual theory of degrees of freedom, acknowledging that the atoms in a molecule of di- or triatomic argon would have to be very compactly and rigidly arranged so that the molecule would have negligible rotational and vibrational energy (see, for example, Brauner, op.cit., and Nasini, op.cit.).

is N_3; Armstrong and Nasini on the other hand felt that argon is diatomic, placing A = 20 in group VIII of the periodic table between F and Na. The opposite tendency, of accepting that $\gamma = 1.66$ indicates monoatomic argon whatever the significance this may have for the periodic law, was shown by, among others, Rayleigh and Ramsay themselves and also Rücker.[127] Rücker is reported by Ramsay's wife as having said at the Royal Society meeting of 31st January 1895, in response to Armstrong's criticism of taking $\gamma = 1.66$ as proof of the monoatomicity of argon against the indications of the periodic law, that "Mendeléef's Table ... was not on a level with the great mechanical laws, and that in the face of such a discovery [sc. of argon with $\gamma = 1.66$] it must be allowed exceptions, or must go".[128]

In Argon, a new constituent of air, immediately after his consideration of the question of the nature of the correspondence of argon to the periodic law, Mendeleev referred to a letter which he had recently received from Ramsay:

> ... on 17th February (old style) I received a letter from Professor Ramsay (dated 25th February, new style) informing me that "the periodic classification entirely corresponds to its (argon's) atomic weight, and even gives a fresh proof of the law of periodicity" judging from the researches of my English friends. But in what these researches consist, and how this agreement of the atomic weight with the periodic law is actually obtained, is not referred to in the letter.[129]

What Ramsay had in mind in this letter to Mendeleev is not clear;[130] however, from what he had said at the Royal Society meeting of 31st January, 1895, it may possibly have been that argon finds a place in group VIII of the periodic table if we take it to be a mixture of two elements of atomic weights of about 37 and 82.[131] On the other hand, Ramsay may have been referring in the letter not to his own views but to those of others in England (such as Armstrong) who held that argon has an atomic weight of 20 and finds a place in group VIII between F and Na.[132]

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[127] Arthur W. Rücker, Professor of Physics, Royal College, London.

[128] See Bibl.117, 129-30; also, see Rücker's own account, Nature, 51 (7th Feb., 1895) 337.

[129] Pr.Ch., R-6 (1895) 754, n.12 (PLBA,468). The date 17th Feb., O.S., 1895, corresponds to 1st March, N.S., 1895.

[130] I have been unable to find the original letter.

[131] See n.88 to the present chapter.

[132] The suggestion that argon has an atomic weight of ca. 20 and occupies a place in the periodic table in group VIII between F and Na had earlier been made by Ramsay himself, but had been rejected by him by the end of 1894 as a result of the value 1.66 which had been obtained for the specific heat of argon gas (see n.88 to the present chapter).

In the concluding footnote (dated 19th March, O.S., 1895) to Argon, a new constituent of air Mendeleev noted Ramsay's recent isolation of argon and helium from the mineral cleveite.[133] He expressed the view that the accumulation of such new results "may, after detailed and diversified researches, considerably increase the stock of chemical knowledge ... and perhaps will serve as fresh confirmation of the 'periodicity' of the elements".[134] Later in 1895 Mendeleev visited London (primarily on metrological business) where he discussed argon and helium with Ramsay, Lockyer and others. A brief report on the impressions he obtained from these conversations, indicating a shift in interest from argon to helium, was given by him at a meeting of the Russian Physico-Chemical Society (Chemistry Section) in November 1895: "The subject [sc. of the nature of argon and helium] has progressed little. There is little material for its solution, and the matter seems particularly obscure as regards argon. Helium offers more interest and more hope for an early elucidation of the question".[135]

Two years later, in a footnote to his article The periodic lawfulness of the chemical elements (R.; written late 1897, publ. 1898), Mendeleev had the following to say about argon and helium:

> In connection with argon and helium ..., although they both undoubtedly exist ... they have so far not entered into a single compound, and we are therefore unable to say what their atomic weights are; ... we know, from their vapour densities, only their molecular weights ... If we consider (on the basis of data on their physical properties) that the molecules of argon and helium contain only one atom, we may suppose their atomic weights to be 39.8 (for argon) and 4.2 (for helium); but full confirmation of this is not possible until we obtain compounds for them, and there is as yet no such basis for entering into detailed discussion about the place of these elements among the others ...[136]

While Mendeleev here seems more ready than in Feb.-March 1895 to accept the possibility of the monoatomicity of the argon molecule, in this same article of 1897-8 he also suggested that perhaps argon should be placed in group VIII of the periodic table between F and Na (in which case its atomic weight would be ca. 20, and argon gas would be diatomic); at the same time he suggested that perhaps helium occupies a place in the first row (the hydrogen row) of the short-form periodic table.[137] He again added that

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[133] Cleveite contains oxides of uranium, lead and yttrium. Helium is present in an occluded state in the mineral, having been produced by the radioactive decay of the uranium. A certain amount of argon, apparently of atmospheric origin, is also present in an occluded state.

[134] Pr.Ch., R-6 (1895) 755 (PLBA, 470).

[135] J.Russ. Phys.-Chem. Soc., 27 (1895) section 1, p.508 (PLBA,457).

[136] Bibl.11, vol. 23, half-vol. 45, 1898, p.315, footnote (PLBA, 249-50).

[137] Ibid., p.320 (PLBA, 263). See Ch. VI, p.381.

"because neither of these [sc. neither argon nor helium] has yet succeeded in entering into combination, any judgment on their relationship to other elements must at present be considered premature, especially as we cannot consider their atomic weights as established with complete certainty".[138] Mendeleev at this time showed no sign of considering complete inertness in certain elements to be a characteristic which might be found to show accordance with the periodic law: he felt that compound-formation was an essential characteristic of all elements, and that the study of the compounds of an element played an essential part in the determination of its atomic weight and place in the periodic system.

There was no mention by Mendeleev in The periodic lawfulness of the chemical elements (R.; publ. 1898) of his preferred idea of Feb.-March 1895 that argon is N_3, and it therefore seems likely that he had already rejected this hypothesis.[139] The idea that argon may be A_6 (A = 6.5), which had been entertained fairly seriously by Mendeleev in Feb.-March 1895, had undoubtedly also been rejected by him by 1898, and probably much earlier: unlike the suggestion that argon is N_3, this latter suggestion A_6 was never even referred to by Mendeleev after Feb.-March 1895.

In April-May 1900 there appeared in the Russian journal Rossia two letters from Mendeleev to the editor, concerning the discovery claimed by Professor A.P. Lidov (Khar'kov Technological Institute) of a carbonaceous gas, produced by combustion, having the density and chemically inactive character of argon. In the first of these letters Mendeleev wrote:

> Because it was Professor Lidov who obtained this gas, and because the properties which he observed are extremely interesting from both a theoretical and a practical point of view, a repetition of this experiment has immediately been started in our laboratory ... Will it not turn out to be a sub-oxide of carbon, i.e. acetylene in which hydrogen is substituted by oxygen?[140]

In his second letter Mendeleev reported that the attempts in his own laboratory to reproduce Lidov's results had failed; and furthermore, that when he had tested a sample of the gas which Lidov himself had sent him in a sealed tube it "was shown to be combustible, with a density lower than that of air ... and its spectrum coincides with the spectrum of illuminating gas ...

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[138] Ibid. (PLBA, 263-4).

[139] In 1902 Mendeleev listed the main reasons which had "long ago" led him to discard the hypothesis that argon is N_3. Some of these reasons drew upon data which were already available before 1898 (see later).

[140] Colls., 15, 633.

without any traces of the lines of argon".[141] Mendeleev consequently concluded that "according to the data known to me there is no correspondence whatever between the gas obtained by Professor A.P. Lidov and the argon of Professor Ramsay".[142] What is particularly interesting about this episode is not the unremarkable conclusion eventually reached by Mendeleev, but the fact that as late as 1900 he was prepared to suggest in print that argon might possibly be a compound of carbon, perhaps "acetylene oxide", C≡C with O. The idea that argon might be a compound had already been relegated to the realms of "low probability" in Mendeleev's comments of Feb.-March 1895 (see p.444), and during the course of the subsequent five years he seems to have shown an increasing inclination towards the view that argon and its analogues constitute a new family of chemical elements rather than new compounds or allotropic varieties of known elements. This picture of Mendeleev's evolving attitude up to 1900 is supported to some extent by his comments (considered above) on helium and argon in The periodic lawfulness of the chemical elements (R.; publ. 1898); but the strongest supporting evidence is provided by a list which he drew up in 1902 giving the reasons which had led him to discard the hypothesis that argon is N_3. Although written in 1902, this account by Mendeleev of his change of opinion concerning the nature of argon is undoubtedly appropriate (at least to a great extent, and probably entirely so) also to 1900: not only does he write in 1902 that he had "long ago" rejected the idea that argon is N_3, but the reasons which he gives draw upon data which were already available, and widely known, by 1900 -

> When ... I first heard of argon and its unprecedented chemical inertness ... I thought it might be a polymer of nitrogen, N_3, ... but I long ago rejected such a view ..., and now consider argon to be an independent elementary substance, as was maintained by Ramsay from the very beginning. Many reasons induced me to change my view, the main ones being: 1) the undoubted assurance that the density of argon is certainly much below 21 and probably only a little more than 19 (that of hydrogen being 1), while the density of N_3 would have to be about 21 ...; 2) helium ... has a density of about 2 referred to hydrogen, and exhibits the same complete chemical inertness as argon, but in this case we can think of no complexity of the molecule in terms of which we could explain the inertness; 3) in neon, krypton and xenon, Ramsay and Travers found a similar inertness, and the explanation which could be used for argon was not appropriate for these substances[143];

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[141] Ibid., 634.

[142] Ibid.

[143] Mendeleev here seems to be forgetting that in 1895 he had suggested fairly seriously that argon may be A_6. Following this pattern we could perhaps explain krypton (mol.wt.84) as being N_6 (6x14 = 84), which might, as in the case of the proposed N_3, be inert if formed from ordinary N_2 with the evolution of sufficient heat.

> 4) the independent peculiarities of the spectra of these five gases, and the complete unchangeability of the gases under the influence of a series of electric sparks, proved that we here have a family of elementary gases, sharply distinguished from all other known elements by their chemical inertness; and 5) the gradual and definite change of the physical properties in dependence upon the density and atomic weight ... strengthens the conviction that here we have simple bodies, whose individuality, in the absence of chemical reactions can be affirmed only from the constancy of physical characteristics.[144]

It is interesting to note that no reference is made here to the value of the specific-heat ratios of the inert gases. In a footnote to point 5 of this list Mendeleev does say that "the opinion that the molecules of argon and its analogues contain only one atom is derived from a comparative study of the physical properties of these gases",[145] and perhaps this is an indirect reference to specific-heat ratios; on the other hand, however, Mendeleev may here have something else in mind (although what this could be is not clear). In the 7th (1902-3) and 8th (1906) editions of Principles of Chemistry Mendeleev did refer explicitly to the specific-heat ratio of argon, acknowledging that its value of 1.67 had been generally taken as an indication of the monoatomicity of argon. However, echoing his remarks of 1895 he added that "we cannot take this as completely proved, because the value of k varies considerably for gases having the same number of atoms in the molecule, and strongly depends upon the temperature-range and, evidently, also upon the store of chemical energy (e.g. for Cl_2 k is smaller than for N_2, CO, etc.)".[146] For Mendeleev the only convincing reason for recognising the inert gases as monoatomic seems to have been the fact, which emerged in 1900, that this assumption corresponds to a satisfactory placing of these elements in the periodic table.

In the spring of 1900 the suggestion was made to Mendeleev by Ramsay (in person, in Berlin) that argon and its analogues be placed in the periodic table in a new group, distinct from group VIII, between the halogen group (group VII) and the alkali-metal group (group I).[147] This idea, which

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[144] Ether (publ. 1903, 1905): PLBA, 488-9.

[145] PLBA, 489.

[146] Pr.Ch., R-7 (1902-3) Ch.V, n.59; R-8 (1906) n.165. For Mendeleev's remarks of 1895 on specific-heat ratios and "chemical energy", see earlier in the present chapter (p.446).

[147] Mendeleev gives the date of this meeting with Ramsay as 19th March, 1895 (see, for example, PLBA, 492, 520). This is probably an old-style date (corresponding to 1st March, N.S.), since it was given in Russian publications; but because it refers to a meeting in Berlin, where the new-style (Gregorian) calendar was already in use, it might possibly be a new-style date.

Mendeleev had apparently not encountered before, was favourably received by him, and he soon came to adopt it himself.[148] In 1902 he wrote:

> Professor Ramsay himself first informed me ... of the position occupied by the argon elements in the periodic system between the halogens and the alkali metals.[149]

> This [sc. idea of placing the argon elements in a new group between groups VII and I] was extremely important for him [sc. Ramsay] as an affirmation of the position of the newly-discovered elements among the other known elements, and for me as a glorious confirmation of the general applicability (obshchnost') of the periodic law. I had said nothing on the numerous earlier occasions when the argon elements had been held up to me as shortcomings of the periodic system, because I had expected that soon we should all see that the converse is in fact the case.[150]

Whether Ramsay in his conversation with Mendeleev in Berlin in 1900 had used the designation "zero" for this new group is not mentioned by Mendeleev. But whether he had or not, such a designation had already been used earlier in this connection by Errera, at a meeting of the Belgian Academy on 5th March, 1900, and over the course of the subsequent year or two had come to be widely adopted. Although before his meeting with Ramsay in Berlin Mendeleev had apparently not encountered the "zero-group" idea for placing the inert gases in the periodic table, he soon came to hear of Errera's earlier contribution, referring to it in 1902 as follows:

> As far as I know, the first mention in the literature of a zero group was made by Errera at a meeting of the Belgian Academy on 5th March 1900 (Académie Royale de Belgique, Bulletin de la Classe des Sciences, 1900, p.160). This placing of the argon family in a zero group is a strictly logical consequence of the idea of the periodic law, and therefore (a placing in group VIII clearly being wrong) has been accepted not only by me, but also by Brauner, Piccini and others.[151]

The placing of the inert gases in a zero group, seen by Mendeleev to represent the "magnificent survival" of the periodic system and the inert gases in what had been a "critical test" for both,[152] was incorporated into the periodic tables published by him in the 20th century, beginning with table 57 (P30) (1902).[153] Argon is included as Ar = 38, even though

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[148] He was, however, still prepared to consider the possibility that argon might be a compound of carbon in his two letters to Rossia shortly after his return from Berlin in the spring of 1900 (see above, pp.457-8).

[149] Pr.Ch., R-7 (1902-3) Ch.V, n.64 (PLSM, 402).

[150] Ether: PLBA, 492, footnote.

[151] Ether: PLBA, 491, footnote.

[152] Ether: PLBA, 490.

[153] In one of Mendeleev's periodic tables of the 20th century, viz. table 59 (P32) given in the body of the text of the 7th (1902-3) edition of Pr.Ch., the zero group is omitted. This is clearly unintended, as is seen both from the text of this 7th edition and from the fact that the other tables given in this edition, tables 57 (P30) and 58 (P31), both contain the zero group.

vapour-density measurements indicated an atomic weight of 39.9. Mendeleev assumed the lower value solely to preserve strict atomic-weight ordering in the periodic table, mistakenly believing that an atomic-weight value for argon lower than that for potassium would in due course be confirmed by experiment (see Ch. VI, p.350).[154]

Like the iron, palladium and platinum elements of group VIII, the inert-gas elements represent a transition between the elements of groups VII and I in the periodic system;[155] but because their particular transitional character is quite unlike that of the iron, palladium and platinum elements, the inert gases had come to be placed not in group VIII but in a distinct group of their own. The designation "zero group" for the group of inert gases had arisen out of a recognition of the apparent complete inertness, or "zero-valence", shown by these elements. From a consideration of transitional character alone it might be thought that the zero group could equally well be placed on the right-hand side of the short-form periodic table (either between groups VII and VIII, or else following group VIII) as on the left-hand side (preceding group I). There are, however, additional considerations which tend to give preference to the latter placing of the zero group. For Mendeleev there seems to have been one fundamental reason for his consistent placing of the zero group to the left of group I in the short-form table (see tables 58, 60, 61, 62 and 64): this may be summarised briefly in the remark that in the ordered set of whole numbers zero precedes 1, and does not follow 8 or come between 7 and 8. The group-numbers in the periodic table possessed a two-fold significance for Mendeleev: there was a chemical significance, the group-number corresponding to the highest valency shown by the elements of the group in their "saline" (or "salt-forming") oxides; and there was also a significance in terms of the structure of the periodic table, such that the group-number was the ordinal number of

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[154] The assumption by Mendeleev in the early 20th century of an atomic-weight value for argon lower than that which was indicated by vapour-density measurements provides an interesting contrast with his tendency in 1895 to consider that the true atomic weight of argon is probably greater than the value indicated by vapour-density measurements (see n.98 to the present chapter, and the quoted passage to which it refers).

[155] In his long-form table 63 (P36) (1906) - unlike the otherwise very similar earlier long-form table 57 (P30) (1902) - Mendeleev included the inert-gas elements twice, with the appended footnote: "In this table the elements of the zero group are placed not only before the first period, but also after the last one, in order to show clearly that they constitute a link in the same way as do the elements of group VIII".

the group in the short-form table. The designation "zero group" for the inert gases, i.e. the ascription to them of the group-number zero, was justified for Mendeleev on chemical grounds by the apparent inability of these elements to form saline oxides or salts, i.e. by the fact that their maximum saline valency appeared to be zero; and since the group-number was also the ordinal number of the group in Mendeleev's short-form table, the inert-gas group must precede group I in this table.[156] Over and above this fundamental reason for Mendeleev's placing of the zero group to the left of group I in his short-form periodic table there were two further factors which could be seen as advantages of such a placing. The first, which was acknowledged by Mendeleev himself, was the scope thus introduced into the periodic table for extrapolation into the pre-hydrogen region (see Ch. VI, p.377). The second such factor was not explicitly referred to by Mendeleev, but nevertheless was undoubtedly important for him, and explains why he never suggested the possibility of heavier analogues of neon in the odd-numbered rows of the short-form table:[157] this was the question of the symmetry of the table. A placing of the inert-gas group on the right-hand side of the short-form table would add to the existing asymmetry in the table caused by the occupancy-pattern in group VIII, but the placing to the left of group I goes some way towards balancing this asymmetry due to group VIII. Thus, despite the triple-occupancy of places in group VIII compared with the single-occupancy shown in group 0, and despite the imbalance between the occupation of the earlier rows (before row 4) in group 0 and the non-occupation of these rows in group VIII, the short-form periodic table nevertheless acquires a certain added degree of symmetry from the placing of the zero group to the left of group I, because the occupancy of group VIII in even-numbered rows only is then balanced by the corresponding occupancy-pattern with respect to the rows which is shown by the elements of group 0 from argon onwards (see, for example, table 58).

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[156] This reasoning is given by Mendeleev himself in various places in his writings of the early 20th century: see, for example, PLBA, 289, 315, 491 and 520.

It should perhaps be emphasised that the present considerations on the placing of group 0 concern the short-form periodic table only. In the long-form table the sub-groups are separated, and consequently there is no single ordinal sequence corresponding to the group-numbers. Moreover, the symmetry advantage (discussed below) in placing the zero group before group I in the short-form table does not apply to the long-form table.

[157] Neon in Mendeleev's short-form tables is placed in a different sub-group from He, Ar, Kr and Xe (see, for example, table 58). The reason for this is clearly not chemical, but is one of symmetry of the table.

While Mendeleev in 1905 acknwoledged that "because of their incapacity for forming saline compounds of the type RX_n" we should place argon and its analogues in a special "zero" group preceding group I in the short-form periodic table, he also wrote at the same time - echoing remarks he had made in the 1890's - that "until we obtain compounds of some sort for them ... we cannot be completely sure of the nature of these gases".[158] Although in this continuing expectation by Mendeleev of compound-formation by the inert gases we might recognise an instinct which has turned out to be correct,[159] in the light of his views on the chemical significance of the group-numbers in the periodic table there is nevertheless perhaps a hint of inconsistency in his expectation of compound-formation for elements whose group-number he accepted as being zero. However, his acceptance of zero-valence (inertness) for argon and its analogues with respect to the formation of saline oxides and salts need not have entailed acceptance of complete inertness with respect to the formation of other types of compound (e.g. peroxides), and it is therefore perhaps such "non-saline" compounds which he had in mind in his comments of the early 20th century in which he anticipated compound-formation by the inert gases. There seem to have been two particular factors which encouraged Mendeleev's continuing expectation in the early 20th century of compound-formation by the inert gases: first, his "chemical" theory of solution, which postulated the formation of unstable chemical compounds between solute and solvent, led him to recognise solutions of the inert gases as already representing compound-formation of a weak and transitory sort - the inert gases "clearly evince the faculty of solution, i.e. of forming indefinite, easily dissociated compounds";[160] and secondly, various minerals had been discovered which contained certain of the inert gases in an apparently stable state of combination.[161] Some of these minerals failed to lose their inert-gas content by mere heating in vacuo, requiring chemical treatment (for example, with hot sulphuric acid) before

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[158] Pr.Ch., R-8 (1906) n.166 (PLBA, 520-1).

[159] Since 1962 various inert-gas compounds have been prepared, e.g. KrF_2, KrF_4, XeF_2, XeF_4, XeF_6, $XeOF_4$ (see, for example, Bibl. 28).

[160] Ether (publ. 1903, 1905): PLBA, 482. For an outline of Mendeleev's theory of solution see Ch. I, pp. 40-1.

[161] These were all uranium minerals, e.g. cleveite (see n.133, above), fergusonite, monazite, uranite, etc. They contain interstitially-entrapped helium (produced by radioactive decay of the uranium) and other inert gases and nitrogen (of atmospheric origin).

the gases were liberated. This led Mendeleev to conclude that the inert gases in these minerals are "not simply in a state of absorption", but are present "in the form of some sort of stable compounds".[162]

With Mendeleev's incorporation of the inert gases into his periodic system as a zero group two missing higher analogues of xenon came to be indicated, at 0 - 10 and 0 - 12 (see Ch. VI, pp.398-9 and 403). Of these two predictions, that for 0 - 10 has turned out to be false, being a consequence of Mendeleev's erroneous extension into the region of the periodic system between Ba and Ta of the pattern of periodicity shown elsewhere in the system; the prediction for 0 - 12 on the other hand has been confirmed, this place corresponding to the inert-gas element radon. Although radon had already been discovered during the early years of the 20th century before Mendeleev's death, as "emanation" from various radioactive substances, Mendeleev never suggested that this "emanation" might actually be a new inert-gas element. Writing about "emanation" in 1905 he concluded that to form a definite opinion about its nature would be premature,[163] although he did note that "Rutherford and Soddy (1903) have shown that emanation ... is chemically inactive like argon".[164]

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[162] Pr.Ch., R-8 (1906) 92-3 (PLBA, 518).

[163] Pr.Ch., R-8 (1906) n.565 (PLBA, 527). (See Ch. II, pp. 98-9).

[164] Ibid.

/ Duncan

CHAPTER VIII

QUESTIONS OF ACHIEVEMENT, IMPACT AND PRIORITY IN THE HISTORY OF THE DISCOVERY AND DEVELOPMENT OF THE PERIODIC SYSTEM; AND AN ASSESSMENT OF THE SIGNIFICANCE OF THE PERIODIC SYSTEM

The following consideration of what may conveniently be labelled "achievement, impact and priority" in the history of the emergence of the periodic system involves an attempt at objective evaluation of the contributions of various scientists towards this emergence, and also presents an account of the attitude of these scientists themselves towards their own and related contributions, and an assessment of the impact of the individual contributions upon the scientific community in general. In attempting to evaluate objectively various contributions in the history of the emergence of the periodic system we shall be concerned with a number of different aspects of these contributions. Such factors as explanatory and predictive power, actual degree of success of predictions, coherence, and connections with other branches of knowledge, will be considered. Gains and losses with respect to earlier work will be assessed; and factors such as the motivation and aims of particular scientists, and the extent of their knowledge of the related work of predecessors, will be taken into account. In considering questions of priority, and especially in assessing the justification of priority claims, it will be necessary to distinguish carefully the different components of a composite contribution, as well as to bear in mind that the very nature of the discovery process is itself complex, involving for example not only the uncovering of something novel but also the recognition of novelty. Apart from those cases where they are the product merely of partiality or historical ignorance, priority disputes frequently seem to be arguments in which the antagonists are at cross-purposes either because they are unwittingly talking about not quite the same discovery, or else because they have different conceptions of what is meant by "discovery".

Already by 1850 discoveries had been made and tendencies had arisen which can be seen as direct precursors of certain discoveries and tendencies associated with the periodic system of the elements[1]: families of analogous elements (e.g. the halogens, the alkali metals) had come to be recognised; a parallelism between different families of elements had been observed, expressed in the "law of triads" (Döbereiner), according to which not only did the various families tend to have the same number of members (viz. three), but for each of these 3-membered families ("triads") there was a common weight-relationship between the members, such that the atomic weight (or

[1] An historical survey of these developments of the first half of the 19th century is given in Ch. III, section B.

equivalent weight) of the middle member was the arithmetic mean of those of the other two members; the weight-relationship between the members of a triad was considered as being not attributable to chance (Döbereiner, Gmelin); the law of triads had led Döbereiner to suggest that Sr may be some sort of mixture or compound of Ca and Ba, to predict the existence of two analogues of F other than Cl, Br and I, and, apparently, to predict successfully the atomic weight of Br; and attempts had been made to construct a single classificatory system which included all elements (Gmelin, 1843; O.W. Gibbs, 1845[2]), although little or nothing had been said about the significance of the particular systems proposed. But while these developments before 1850 can now be recognised as being of significance for the emergence of the periodic system, they attracted little attention at the time; and the little attention they did attract was not always favourable, as is seen for example from a scornful remark about Döbereiner made by Berzelius in 1821.[3] Moreover, these early developments were on a very small scale compared with the rapid expansion which occurred in this and related fields during the 1850's.

The 1850's saw the doctrine of triads first greatly extended in scope, and then ultimately rejected in favour of the more flexible ideas of family-membership which had begun to emerge. The first hints appeared of the idea of sub-groups existing within larger family groups. A parallel was drawn between the weight-relationships within families of chemically-similar elements on the one hand, and within homologous and polymeric organic series on the other, and this was taken to indicate that the chemical elements are composite. Algebraic formulae were proposed for expressing the series of atomic weights (equivalent weights) within the chemical families. Various types of relationship between the different chemical families came to light. Further attempts were made to construct a single classificatory system for all elements; and a related development was the search for regularities and irregularities in the series of all elements arranged in the order of increasing atomic (equivalent) weight. The question again arose, as it had earlier for Döbereiner and Gmelin in connection with the triads, as to whether the observed relationships among the elements could be taken as being fortuitous, or whether they represented some fundamental law of connectedness. Finally, the observed regularities were used as grounds for predicting the

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[2]Concerning the contribution of O.W. Gibbs, see Ch.III, n.153.

[3]"Thomson has no common sense in chemistry. I do not know whether he or Döbereiner in Germany is the worst chemist existing at this moment" (see Ch.II, n.32).

existence of new elements, and for predicting atomic-weight values, again following the tendency shown earlier by Döbereiner. Certain specific examples of such developments are discussed below.[4]

A major influence in promoting these extensive developments of the 1850's was the address given by Dumas at the Ispwich meeting of the British Association in 1851. In this address Dumas discussed triads, suggesting (as had Dobereiner for the particular case of Ca, Sr, Ba) that the middle member may be somehow composed of the other two, and pointing to the possibility of predicting the existence of an unknown middle element of a triad if the two extreme elements happened to be known. Dumas' Ipswich address soon produced a great stir among chemists, stimulating the subsequent decade of intense activity along the same or related lines; for this reason it must be seen as a seminal contribution in the history of the emergence of the periodic law. In retrospect we can find great foresight in Faraday's remark of 1852 that the ideas expressed in 1851 by Dumas "possibly may be the harbinger of a new law ... We seem here to have the dawning of a new light, indicative of the mutual convertibility of certain groups of elements, although under conditions which as yet are hidden from our scrutiny".[5] Dumas' contribution of 1851 was explicitly acknowledged in articles on atomic-weight relationships by, for example, Gladstone (1853) and Cooke (1854): Cooke wrote, "Numerical relations between the atomic weights of the chemical elements have been very frequently noticed by chemists. One of the fullest expositions of these relations was that given by M. Dumas in Paris, before the British Association for the Advancement of Science, at the meeting of 1851".[6] In addition to stimulating the researches of the 1850's in the field of atomic-weight relationships by his British Association address of 1851, Dumas also played a significant part in subsequent developments in this field, particularly during the period 1857-9; and it is primarily for this latter contribution that he came to be recognised by all of the principal participants in the actual discovery of the periodic system (de Chancourtois, Newlands, Odling, Hinrichs, Lothar Meyer and Mendeleev) as one of their foremost precursors.

Compared with the work of the 1860's from which the periodic system directly emerged, and which in general seems to have been motivated primarily

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[4] An historical survey of these developments of the 1850's is given in Ch.III, section B.

[5] A course of six lectures on the non-metallic elements (Royal Institution), London, 1852, pp. 158-60.

[6] Cooke, Amer. J. Sci., 1854, p.387 (see Ch.III, n.67). For Gladstone's acknowledgment of Dumas' contribution of 1851 see Ch.III, p.122.

by the desire for a single "natural" classificatory system for all chemical elements (in more than one case in a pedagogical context), much of the precursory work on atomic-weight relationships which took place during the 1850's tends to have been concerned more with the question of the possible complexity of the elements, in this respect showing an affinity with Proutian-type traditions. (Exceptions to this generalisation are perhaps provided by the work of Gladstone, 1853, which shows much of the spirit of the classificatory activities of the 1860's, and the work of Hinrichs, 1864-9, which often appears to be more in the spirit of the 1850's[7]; also, although the contributions of Lothar Meyer during the 1860's and early 1870's were certainly motivated by the search for a classificatory system, Meyer was still very much concerned with the problem of the complexity of the elements). However, it seems to have been not this difference in primary motivation which delayed the emergence of the periodic system until the 1860's, nor the slightly smaller number of elements known and the somewhat less developed state of knowledge of their chemical properties during the 1850's, bur rather the general lack of appreciation of the distinction between atomic weight and equivalent weight which persisted until Cannizzaro's clarification of the subject at the Karlsruhe Congress of 1860[8]. In the

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[7]According to Hinrichs himself, his Atomechanik (publ. 1867) was in fact written in 1855 (see Ch.III, p.147). If this claim is true, some of Hinrichs' work is not only in the spirit of the 1850's, but actually of the 1850's. However, the fact that the atomic-weight values employed by Hinrichs in his Atomechanik are evidently based upon the clarified concept of atomic weight presented by Cannizzaro in 1858-60 sheds considerable doubt upon the claim that the Atomechanik dates from 1855.

[8]Of course, developments in the fields of discovery of elements and knowledge of chemical properties did help to stimulate the emergence of the periodic law, but these factors do not appear to have been crucial in this respect.

During the period 1850-70 the following elements were discovered: Cs (1860), Rb (1861), Tl (1861), In (1863) and solar helium (1868). The total number of elements known at this time was about 60.

Some years later, in 1889, Mendeleev in his Faraday lecture was to list as one of "three series of data without the knowledge of which the periodic law could not have been discovered, and which rendered its appearance natural and intelligible", the "accumulation by the end of the 1860's of new information concerning rare elements" such as Nb and V, "which disclosed their many-sided relations among themselves and to other elements" (PLBA, 210-3). While Mendeleev here perhaps rather overstates the importance of this "rare-element" series of data for the emergence of the periodic law, such data were certainly of some significance in this respect. (The other two "series of data" listed at the same time by Mendeleev were the new system of atomic weights which had been established on the basis of the ideas presented by Cannizzaro at the Karlsruhe Congress in 1860, and the various contributions which had been made during the 1850's and 1860's to the study of atomic-weight relationships).

studies which were made on weight-relationships among the elements before 1860 (and even in some which were made shortly afterwards) the characteristic weights used were either equivalent weights, or else they represented some hybrid of equivalents and true atomic weights. Such values could bring out certain relationships within the chemical families, and in some cases even between families, but they did not provide a suitable basis for establishing a single all-embracing system of relationships among the known elements. Such a basis was provided by Cannizzaro at the Karlsruhe Congress, which, like the British Association meeting of 1851 at which Dumas spoke, must therefore be seen as having played a major role in the history of the emergence of the periodic system.

That the inadequate state of knowledge of atomic weights before 1860 was the crucial factor in delaying the discovery of the periodic law until the 1860's is perhaps seen most clearly from Gladstone's work of 1853. In 1853 Gladstone published a paper in which he arranged the chemical elements (56 in number) into a single series in order of increasing "atomic weight".[9] But the set of values he used for these "atomic weights" in fact represents a hybrid of equivalents and true atomic weights, and as a result the periodicity of the elements was not apparent from this ordered series: Gladstone's observation on the series was that "we notice some peculiarities, but no very striking ones",[10] the peculiarities referred to being associated with clustering and spacing of the atomic-weight values in the series. However, had Gladstone taken these same 56 elements, and used throughout atomic-weight values based upon the same empirical equivalent-weight values as were the "atomic weights" he actually used, but which correspond instead in all cases to the correct multiples of these equivalents from the point of view of Cannizzaro's concept of atomic weight, then it is difficult to believe that he could have failed to observe the periodic recurrence of analogous elements in the series, especially for the earlier part of the series. To speculate even further: since Gladstone in 1853 seems to have been attracted towards the idea of a single "natural" classificatory system for all elements, as indicated by his adoption (for want of a better alternative) of Gmelin's V-shaped system in the very paper in which he presented his ordered series of 56 elements, it is perhaps likely that had he observed a periodicity of properties in the ordered series of elements he would have attempted to draw up a classificatory system based upon this periodicity, i.e. a periodic system. It is interesting to compare Gladstone's paper of 1853 with two papers

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[9] See Ch.III, pp. 121-2.

[10] Loc.cit. (see Ch.III, p.122).

published in 1864 by Newlands (July) and Odling (October).[11] These three papers begin in very much the same fashion, with a list of the elements arranged in the order of increasing "atomic weight"; but whereas the hybrid values used by Gladstone give a series of elements showing "no very striking peculiarities", the post-Cannizzaro values employed by Newlands and Odling give a series (the same in both cases[12]) on the basis of which each of these scientists was able to construct a rudimentary periodic system. In their papers of 1864 Newlands and Odling did not recall Gladstone's earlier work; in an article of 1857 Odling had mentioned Gladstone's paper of 1853, but only in connection with the latter's observations on the types of weight-relationship to be found within families of chemically-analogous elements, making no reference to Gladstone's ordering of the elements into a single series on the basis of "atomic-weight" value.[13] Mendeleev (in 1871 and later) mentioned Gladstone's work, but again only in connection with the latter's contribution to the study of weight-relationships within the different chemical families.[14] In general, none of those who in the 1860's were directly involved in the discovery of the periodic law, or those who in the subsequent part of the 19th century were to take part in discussions of achievement and priority in connection with this discovery, appear to have appreciated that Gladstone's approach in his paper of 1853 would quite probably have resulted in his discovery of the periodic law had he been able at the time to appreciate fully the distinction between atomic weight and equivalent. What at first sight is perhaps a particularly puzzling aspect of the affair is that Gladstone himself, who attended the Karlsruhe Congress of 1860, seems to have made no attempt afterwards to reappraise his earlier work on atomic-weight relationships in the light of Cannizzaro's clarification of the concept of atomic weight, not even after Newlands and Odling had begun to arrive at a recognition of the periodicity of the elements in 1864. But it is probable that like many other scientists Gladstone had by the 1860's become disillusioned with the subject of atomic-weight relationships, which after a decade of intensive investigation following 1851 seemed to have produced almost nothing but a mass of unexplained and apparently useless isolated numerical regularities; and that by the 1860's he was therefore blinded to the possibility that certain of the approaches used during the

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[11] For references see Ch. III, nn. 119 (Newlands) and 135 (Odling).

[12] Both Newlands and Odling had adopted the atomic-weight values given by Williamson, op.cit. (see Ch.III, n.118).

[13] Odling, 1857, op.cit. (see Ch.III, n.70), p.424, footnote.

[14] See, for example, PLBA, 387 (1871), 211 (1889) and 314 (1906).

1850's - including his own of 1853 - might still turn out to have fruitful results. Even when confronted at a meeting of the Chemical Society in 1866 with Newlands' "law of octaves" and the essentially "periodic" classificatory system which Newlands had based upon it, Gladstone appears to have been more critical than appreciative.[15]

Of the various other types of contribution during the 1850's to the study of atomic-weight (equivalent-weight) relationships, there were two which, like Gladstone's atomic-weight ordering of the elements, appear to have come particularly close in spirit or achievement (or both) to the subsequent activities associated with the actual discovery of the periodicity of the elements: these were on the one hand the various contributions towards the study of the relationships not just within the different chemical families but also between the families, and on the other hand the attempts which were made to predict the existence of unknown elements and determine atomic-weight values by interpolation and extrapolation of observed regularities. Whereas the potential of Gladstone's method of ordering all of the elements according to atomic weight lay in the direction of a recognition of the periodicity of the elements prior to the construction of any "periodic" classificatory system, the more common tendency of the 1850's to seek relationships between the different chemical families represented a path to the discovery of the periodicity of the elements by way of the direct building-up of a periodic system from its constituent families. The attempts which were made during the 1850's to predict unknown elements and the values of atomic weights are of interest for the history of the periodic law perhaps primarily in that they - like Döbereiner's earlier attempts at prediction, and the subsequent attempts by Newlands in the 1860's - represent an anticipation of Mendeleev's famous practice of using the periodic system for prediction.

Those who concerned themselves in the 1850's with the question of relationships between different chemical families include Cooke (1854-5), Kremers (1856), Lenssen (1857), Odling (1857), Dumas (1857-9) and Mercer (1858). The contributions of Kremers and Lenssen in this field showed strict adherence to the concept of triads, the resulting systems of correlated triads ("conjugated triads", Kremers; "enneades", Lenssen) representing not so much a development towards a periodic system as an extension of the doctrine of triads in another direction.[16] This seems to be especially the case for Kremers' triplet of cubic triads, which from the present standpoint

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[15] See Ch. III, pp. 138-9.

[16] The contributions of Kremers and Lenssen are outlined in Ch.III, pp. 121 and 123-4.

may be seen as representing the limit of a "blind-alley" deviation from the developments which led to the emergence of the periodic system. We should, however, recognise at the same time that Kremers' triplet of conjugated triads not only is the product of an admirable dedication to the development of a not unsuccessful idea (viz. the idea of triads) to some sort of limit, but also possesses an appealing simplicity, and, furthermore, seems to be the only classificatory system of the 19th century to incorporate a definite prediction about the total number of chemical elements (viz. $3^4 = 81$, a number which in the historical context would seem quite a reasonable suggestion, since about 60 elements were actually known at the time). The related but less fully developed classificatory work of Lenssen is of interest in the study of the emergence of the periodic system mainly for the manner in which the enneades were used to determine "atomic-weight" values for certain known elements, notably for "erbium" and "terbium".[17] The method employed was an extension to two dimensions of Döbereiner's earlier use of the triad-relationship for prediction, and as such was essentially already the method of interpolation/extrapolation used by Mendeleev for prediction on the basis of his idea of "atomanalogy" in the periodic system[18]: Mendeleev's periodic system can therefore be seen to incorporate two remnants of the doctrine of triads - this idea of "atomanalogy", and also the triple-occupancy of places in group VIII (viz. by Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt). But although certain features of the doctrine of triads were thus retained in later work, the contributions of Kremers and Lenssen represented the last of the classificatory approaches which maintained strict adherence to the triad concept. Even at the time when Kremers and Lenssen were presenting their ideas the triad concept was already being superseded by more flexible ideas of family-membership which recognised natural families of elements containing more than three members. It was in this latter spirit that the work of Cooke, Odling, Dumas and Mercer during the period 1854-9 was carried out.

Cooke's idea of the "affiliation of the series" (1854) was an important step along the path towards the periodic system[19]. As Venable has subsequently remarked (1896), "Cooke caught a glimpse of one great truth, and that was that we must not merely separate out here and there so-called related

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[17] See p.124.

[18] Mendeleev's concept of "atomanalogy" is explained in Ch. V, pp. 320-1.

[19] See Ch.III, p.123.

elements, but must grasp the fact that there is a relationship even between apparently dissimilar elements".[20] In Cooke's work of 1854 we also see the first hint of the recognition of sub-groups (his "sub-series") within larger family groups (this idea seems not to reappear clearly until 1864, when it is found in more fully developed form in the work of Odling). In 1857 Odling recognised a "curious numerical sequence" (viz. the sequence 4, 3, 2, 1) in the valencies of the lowest members of the carbon, nitrogen, oxygen and fluorine groups.[21] But probably the closest approach to the periodic system during the 1850's through the recognition of relationships between different chemical families was Dumas' contribution of 1858, which spoke of a classificatory system which brought out a "double parallelism" of the families[22]. Dumas' description of such a classificatory system seems, as far as it goes, to correspond to Mendeleev's short-form periodic table, even to the extent of including an account of analogy within the system which corresponds closely to what Mendeleev expressed by the term "atomanalogy". But this contribution by Dumas must nevertheless be considered as falling somewhat short of the final attainment of a periodic system of the elements, for three reasons: first, Dumas did not actually present an example of the type of classificatory system which he had in mind; secondly, he did not indicate the particular order in which he envisaged the various chemical families to be arranged in such a system; and thirdly, he spoke only of "metals" in his discussion of the system, not of "elements" (however, it appears from his discussion that this may well have been no more than linguistic laxity, that he was actually using the term "metals" loosely to denote elements in general). Mercer's related contribution of 1858 was less extensive in scope than that of Dumas, but it did include a schematic "table of the atomic parallels" between the oxygen, magnesium, nitrogen and fluorine families.[23]

Like Gladstone, who had also come close to discovering the periodicity of the elements during the 1850's (although from quite a different direction), Dumas played no part in the actual discovery of periodicity which was made in the subsequent decade. He had attended the Karlsruhe Congress, but only the second half of it, missing Cannizzaro's speech and much of the discussion of Cannizzaro's proposals. On the final day of the Congress he had made the

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[20] Bibl.124, p.43.

[21] See Ch.III, p.125.

[22] See Ch.III, pp.125-6.

[23] See Ch.III, p.126.

suggestion (objected to by many of the delegates) that Cannizzaro's atomic weights be used only in considering organic compounds, and the old values retained in inorganic chemistry.[24] That Dumas at this early stage failed to appreciate the special value of Cannizzaro's ideas is not particularly surprising[25]; what is surprising, however, is that nearly nine years later he had apparently still not adopted Cannizzaro's concept of atomic weight, talking in his Faraday lecture (17th June, 1869) of "magnesium, calcium, iron, whose respective atomic weights are 12, 20, 28".[26] Whatever the reason for this retention by Dumas of the old pre-Cannizzaro "atomic-weight" values,[27] the fact that he had still not rejected these old values in 1869 explains why he played no part in discovering the periodicity of the elements during the 1860's. Of the many who had investigated atomic-weight relationships during the 1850's, it seems that only Odling also contributed directly to the eventual discovery of the periodicity of the elements in the 1860's.[28]

Whereas Kremers in 1856 had predicted the existence of about 20 unknown chemical elements without discussing their probable atomic-weight values, and Lenssen in 1857 had determined "atomic-weight" values for known elements, Carey Lea in 1859-60 (pre-Karlsruhe) used certain regularities in atomic-weight relationships to predict both the existence and the atomic-weight values of two unknown elements: an analogue of Ag and Au of atomic weight 152.5, and an analogue of Sb and Bi of atomic weight 164.[29] Elements of such atomic weights have in fact subsequently turned out to exist, viz. Eu = 152 and Ho = 164.9; but since these are both rare-earth elements, in no significant way analogues of Ag or of Sb, they cannot be regarded as fulfilling Carey Lea's predictions. Carey Lea's main contribution towards the discovery of the periodic law was probably his suggestion that vanadium be included in the nitrogen group of elements.

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[24] See Ch.III, p.116 (from Mendeleev's report of the Karlsruhe Congress).

[25] After all, Lothar Meyer, who had attended the whole of the Karlsruhe Congress was apparently only convinced of the truth of Cannizzaro's views on reading a copy of the Sunto shortly afterwards; and Odling, who was also at the Congress, did not adopt Cannizzaro's atomic-weight values until 1864.

[26] Chem. News, 20 (1869) 1-7; p.5.

[27] The reason is undoubtedly to be found partly in Dumas' much lesser involvement in chemistry during the 1860's because of his activities as a Senator and as an administrator also in various other respects.

[28] It is possible that Hinrichs might have studied atomic-weight relationships during the 1850's as well as having contributed directly to the discovery of the periodic law during the 1860's (see n.7, above).

[29] See Ch.III, pp.127-8.

With the clarification of the concept of atomic weight by Cannizzaro at the Karlsruhe Congress in 1860, and with the state of discovery of the chemical elements being at the time what it was (viz. with the great majority of elements lighter than barium already known, but with most of the rare-earth elements yet to be discovered[30]), the discovery of the periodicity of properties of the elements now became not only possible but extremely likely. And indeed, in the course of the subsequent decade various representations of this periodicity appeared in the work of at least six scientists - de Chancourtois (France, 1862-3), Newlands (England, 1864-6), Odling (England, 1864-5), Hinrichs (U.S.A., 1866-9), Lothar Meyer (Germany, 1864-70) and Mendeleev (Russia, 1869-71). All six of these workers constructed classificatory systems which illustrate to a significant degree the periodic recurrence of similar characteristics when all (or at least the majority) of the known elements are arranged in the order of increasing atomic weight (see Chs. III and IV), i.e. they all constructed what can justifiably be considered as prototype "periodic systems".[31]

Odling, Mendeleev and Lothar Meyer had attended the Karlsruhe Congress; Odling had even read a paper at the Congress, emphasising that an element cannot have more than one atomic-weight value. Mendeleev appears to have become convinced of the truth of Cannizzaro's views on atomic weight directly

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[30] The fact that only relatively few rare-earth elements were known in the 1860's (see Fig. VII-1, p.409), and that not even all of these had been characterised with any accuracy, was undoubtedly advantageous for the discovery of the periodic law: if all or many of the lanthanide elements had been well-characterised at this time it would have been more difficult to have detected a periodicity of properties for the elements. (This point has also been made by Spronsen, Bibl.110, p.260).

[31] As suggested here, there would seem to be three requirements which need to be satisfied to a significant degree before we can acknowledge any particular classificatory system of the elements constructed in the era of emergence of the periodic law as having attained the level of a periodic system, viz. the ordering of the elements according to atomic weight, the representation of the regular recurrence ("periodicity") of properties which accompanies this ordering, and the incorporation of all of the elements in a single system. No periodic system has ever satisfied all of these requirements completely (in fact, correspondence with the modern periodic system, based as it is upon atomic-number ordering rather than atomic-weight ordering, actually entails contravention of the principle of strict atomic-weight ordering in a few particular cases), and there is no clear-cut level of significance to which the requirements must be satisfied before attainment of a periodic system can be recognised. Judgments of this question are based upon considerations of degree rather than of kind, and contain an unavoidably arbitrary element.

from the contributions of the latter chemist at the Congress itself. Meyer's understanding and acceptance of these views apparently came not so much from the actual Congress as from reading a copy of Cannizzaro's Sunto immediately afterwards. Both Mendeleev and Meyer had therefore already accepted the new atomic-weight system by the end of 1860, about 4-5 years before it can be considered to have gained widespread acceptance. The reason for the particularly ready acceptance of Cannizzaro's ideas by Mendeleev was undoubtedly the fact that Mendeleev had himself been working along very similar lines during the late 1850's: Cannizzaro's contribution at Karlsruhe merely served to crystallise Mendeleev's own incompletely-formed ideas on the subject of atomic weights.[32] Unlike Mendeleev and Meyer, Odling did not adopt Cannizzaro's system until 1864[33] - in 1863 he had still maintained that "the objections to Cannizzaro's general proposition, are ... too great to admit of its adoption".[34] Odling's adoption of Cannizzaro's values seems to have been influenced by Williamson.

De Chancourtois (who was a mineralogist and geologist, not a chemist), Newlands (at the time fighting under Garibaldi) and Hinrichs (completing his studies at Copenhagen University prior to leaving for the U.S.A. in 1861) did not attend the Karlsruhe Congress. The "characteristic numbers" (or "numerical characteristics") used by de Chancourtois in 1862-3 nevertheless for most elements correspond closely to the atomic weights of Cannizzaro,[35] which is a little surprising in the work of a non-chemist who had not been at Karlsruhe, at a time when Cannizzaro's atomic weights were still not in general use.[36] Newlands came to adopt Cannizzaro's values in

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[32] See Ch.III, p.117.

[33] See Ch.III, pp. 140-1.

[34] Loc.cit. (see Ch.III, p.140).

[35] See Ch.III, p.129. In addition to the Cannizzaro-type atomic-weight values, we find ascribed to certain elements in de Chancourtois' vis tellurique also "secondary characteristics" (see Ch.III, p.132), which seem to represent not possible alternative atomic-weight values, but additional values. This inclusion of "secondary characteristics", which were derived from specific-heat data on the simple substances, would appear to indicate a degree of failure on the part of de Chancourtois to appreciate the distinction between "element" and "simple substance". We cannot see in these "secondary characteristics" an anticipation of isotopes, because the "secondary characteristics" are appreciably different in value from the ordinary "characteristic numbers", the two values for the elements concerned corresponding to quite different regions of the vis tellurique (e.g. the two values for carbon are 12 and 44).

[36] A similar point has been made by Hartog, Bibl.26, p.188.

1864, through the influence of Williamson. The "atograms" or "atomic numbers" used by Hinrichs in his contributions of 1867-9 were evidently based upon Cannizzaro's values, although these latter were doubled in accordance with Hinrichs' adoption of the weight of his assumed ultimate "panatom" (= $\frac{1}{2}$H) as unit.

De Chancourtois' work on the vis tellurique was prompted by a desire to find a classificatory system of the elements which could serve as a basis for his lithographical studies (de Chancourtois seems to have been a systematist by nature). The motivation which led Meyer and Mendeleev to their periodic systems also appears to have been the desire to establish a natural classification of the elements, but in their cases within a pedagogical context, in the course of their preparation of chemistry textbooks.[37] The studies which led Newlands and Odling to the construction of periodic systems were attempts at extending the work of the 1850's on atomic-weight relationships and the classification of the elements: in Odling's case, as for Meyer and Mendeleev, we find a pedagogical application of the resulting classificatory system, his table being included both in his Course of Practical Chemistry (1865) and in Watt's Dictionary of Chemistry (1865) (in Odling's case, however, unlike the cases of Meyer and Mendeleev, the table was given a pedagogical application only after a discovery process which seems not to have been pedagogically motivated). Hinrichs' main concern in his classificatory work of the 1860's was clearly the furtherance of his ideas on primary matter.

All six of these scientists in whose work during the period 1862-70 appeared representations of the periodicity of the elements were already aware of precursory contributions which had been made during the 1850's concerning atomic-weight relationships and the classification of the elements.[38] They all acknowledged at the time the earlier work of Dumas, and most of them acknowledged also other precursors of the 1850's: Mendeleev, for example, in his first publication on the periodic law (1869) mentioned by name in this respect Kremers, Lenssen, Dumas, Pettenkofer and Sokolov.[39] As

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[37] Meyer, Bibl.80, 1864; Mendeleev, Bibl.65, 1869-71. An account by Mendeleev himself of what led him to attempt a classification of the chemical elements, written in 1869, is quoted in Ch.III, p.162.

[38] Odling, unlike the other five (except possibly for Hinrichs - see n.7, above), had himself been a "precursor" during the 1850's.

[39] See Ch.III, p.161. In Pr.Ch., R-8 (1906), Mendeleev wrote that "in my construction of the periodic system of the elements I made use of the work of previous investigators: Dumas, Pettenkofer, Kremers and Lenssen" (PLBA, 314). In his writings of 1871 (Berichte, Annalen) and 1889 (Faraday lecture) he mentions also Gmelin, Cooke, Odling (1857) and Strecker as precursors (see PLBA, 106, 211-2, 387), but whether he knew of their work before he drew up his first periodic system in 1869 is not clear.

far as is known, however, none of the six compilers of prototype periodic systems during the period 1862-70 began his work in this direction with any knowledge of the related activities of the other five. This is obviously the case for de Chancourtois, whose contribution was historically prior to those of the others. The conclusion of such initial independence for the work also of Newlands, Odling, Hinrichs, Meyer and Mendeleev is based upon the claims to this effect subsequently made by some of these scientists on their own behalf,[40] and upon the lack of any definite evidence to the contrary. But since autobiographical claims and an absence of counter-evidence are not the most reliable grounds upon which to base judgment, it should be borne in mind that further research may possibly lead us to reject this conclusion of initial independence in certain cases. In fact, there are a few areas where such research might seem to be particularly invited: thus, the simultaneous development of "periodic" classificatory systems by Newlands and Odling in England in 1864-5 perhaps merits deeper investigation than it has so far received, in view of the clear possibility of some direct or indirect mutual influence; also, that Hinrichs apparently followed the Comptes Rendus with much interest, publishing a number of papers in it,[41] raises the question of whether he may perhaps have seen de Chancourtois' publications on the vis tellurique; and finally, the combination of facts that in 1862 Mendeleev had shown enough interest in Odling's work to obtain a copy of his Manual of Chemistry (1861), that in 1867 had been published a Russian translation (by Savchenkov) of Odling's Course of Practical Chemistry (1865) which contained a "periodic" table of "Atomic Weights and Symbols", and that Mendeleev's own "attempt at a system" (1869) resembled Odling's table to an appreciable degree, cannot but leave the slight feeling that perhaps Mendeleev had come across Odling's 1865 table before 1869 and had not remembered this when he explicitly stated the contrary in a note appended to his first article on the periodic law.[42] But whatever may turn out to be shown by future research,

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[40] See, for example, Mendeleev's claims of initial independence given in Berichte (1871) (PLBA, 386-90), Berichte (1880) (PLBA, 396-405) and Pr.Ch., R-8 (1906) (PLBA, 314).

[41] See Zapffe, Bibl.135.

[42] Mendeleev's interest in 1862 in Odling's Manual of Chemistry is apparent from the contents of a letter of 1862 from N.P. Il'in to Mendeleev (see pp. 29-30 of the typescript work by A.V. Skvortsov entitled Dnevniki D.I. Mendeleeva, 1855-1887, to be found in MALU). Concerning Mendeleev's note in Correlation of properties (1869) on the subject of Odling's 1865 textbook table, see Ch.III, p.161.

it seems reasonable on current evidence to accept that the work of de Chancourtois, Newlands, Odling, Hinrichs, Meyer and Mendeleev which led each of these scientists during the period 1862-70 to draw up what can be recognised as prototype periodic systems, was begun in each case in complete ignorance of the related work of the other five. This does not necessarily mean, however, that all six can be recognised also as having arrived independently at their first prototype periodic system. To form a judgment on this latter question we must first consider how long the initial independence of the various contributions lasted, and at what stage in the work of each of the six contributors we can recognise the achievement of construction of a prototype periodic system.

A knowledge of the related work of one or more of the others was in fact fairly soon gained by certain of these six contributors. Thus, less than two months after Mendeleev in Feb./March 1869 had constructed his "attempt at a system" his attention had been drawn by Savchenkov to the similar table in Odling's Course of Practical Chemistry (1865); when Lothar Meyer wrote his article The nature of the chemical elements as a function of their atomic weight (G.; publ. March 1870) he already knew something of Mendeleev's work of 1869, including the "attempt at a system"[43]; and Mendeleev's contributions after March 1870 were made in the knowledge of Meyer's work.[44] As regards Newlands and Odling, it is very unlikely that they did not fairly soon learn of each other's related work: Newlands' claim in 1866 of priority of discovery of the "law of octaves" was probably a move to pre-empt any possible (but as it turned out, not forthcoming) claim of priority in this connection by, or on behalf of, Odling. But since Mendeleev's "attempt at a system" would seem to come close enough to being an all-embracing system of elements in which is shown a fairly regular recurrence ("periodicity") of similar properties with increasing atomic weight to justify its recognition as a prototype periodic system, and since Newlands and Odling had both already drawn up recognisably "periodic" classificatory systems in 1864,[45] the facts of Mendeleev's being told of

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[43] See Ch.III, p.152.

[44] See Ch.III, pp.170-1.

[45] Spronsen (Bibl.110) considers Newlands' system of August 1864 (see Fig. III-3) to be a periodic system, but not Newlands' system of July 1864 (see Fig. III-2). On the basis of the criteria given in n.31 of the present chapter, however, it would seem justifiable to recognise Newlands' system of July 1864 as already representing a crude periodic system.

Odling's work in April 1869 and of Newlands' probable knowledge of Odling's work (and vice versa) by 1866 provide no grounds for questioning the independent initial construction of prototype periodic systems by Mendeleev, Newlands and Odling. The historical priority of de Chancourtois' vis tellurique, and the fact that whether or not we recognise Hinrichs' circular system of 1867 as already being a periodic system[46] he had apparently still not learned of the related work of any of the other five contributors when he presented his clearly "periodic" systems of 1869, leads me to acknowledge independent construction of prototype periodic systems also for de Chancourtois and Hinrichs. In the case of Lothar Meyer, however, this question is more difficult to decide.

The tabular system presented by Lothar Meyer in his 1870 paper (see Fig. III-14) is undeniably recognisable as a periodic system; but, as we have seen, it was drawn up when Meyer already knew of Mendeleev's "attempt at a system". Meyer's only previous published classification of the elements appeared in 1864 in his Modernen Theorien der Chemie (see Fig. III-12). This earlier attempt at classification certainly seems to have been made independently of any related contributions of the 1860's[47], but it is not easy to decide whether it should be acknowledged as representing a periodic system. Meyer's 1864 classification consisted of two separate tables - a main table of 28 elements (see Fig. III-12a), and a supplementary table of 22 elements (in two parts, 6 elements + 16 elements: see Fig. III-12b). In 1868 Meyer drew up a manuscript table (which he never published[48]) in which the main and supplementary tables of 1864 are combined into a single system (see Fig. III-13): this also seems to have been drawn up independently of the knowledge of any similar work by others. Mendeleev, writing in a polemical vein in 1871, dismissed Meyer's 1864 classification as being no more than "a simple collocation of groups of analogous elements".[49] This is certainly unfair to Meyer. Far from being

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[46] Spronsen (Bibl.110, p.122) considers that Hinrichs' 1867 circular system (see Fig.III-9) "may justifiably be called periodic: all the elements occur in groups (genera) and a mutual relationship is established among almost all the elements". However, this "mutual relationship" is not so clearly one of periodic recurrence of analogues with increasing atomic weight that I can unreservedly agree with Spronsen's conclusion.

[47] Meyer seems not to have been aware of de Chancourtois' work, and the other related contributions of the 1860's came after Meyer had drawn up his 1864 classification.

[48] This table was first published by Seubert, 1895 (Bibl.67, p.13).

[49] Mendeleev, Zur Frage über das System der Elemente, Berichte, 4 (1871) 348-52; p.352 (PLEA, 390).

in "simple collocation", the six groups of analogous elements in Meyer's main table of 1864 are arranged in the order of increasing atomic weight[50], and atomic-weight ordering is a noticeable (though not all-pervading) feature even of the supplementary table; furthermore, there is a definite indication in the system, in terms of atomic-weight differences, of a regular recurrence of similar properties with increasing atomic weight.[51] However, there is no indication either in the 1864 classification itself or in the text accompanying it of any attempt or desire to unite the separate tables into a single system[52]; and for this reason I am led to consider Meyer's classificatory attempt of 1864 as having not quite attained the level of what can be acknowledged as a periodic system.[53] This failing of the 1864 classification would seem to have been sufficiently rectified in Meyer's 1868 manuscript system to warrant the recognition of this subsequent attempt as indeed representing a prototype periodic system.[54] Consequently, on the basis not of any published contribution but only of this unpublished 1868 attempt at classification, I acknowledge Meyer as a sixth independent compiler of a periodic system.

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[50]The double-tiering of Meyer's main table in his Modernen Theorien (1864), presumably necessitated by restrictions of space, does perhaps make the atomic-weight ordering less immediately obvious than if all six families had been arranged on the same level.

[51]Meyer himself, writing in (belated) response to Mendeleev's polemical remarks of 1871, claimed that a "candid scrutiny" of his 1864 tables would show "something more than a 'simple collocation of groups of analogous elements' - namely, the endeavour to arrange bodies according to the magnitude of their atomic weights, and to show that chemical value varies regularly in accordance with atomic weight" (Chem. News, 41, 1880, p.203; from Berichte, 13, 1880, p.259).

[52]In 1880 Meyer was to claim in connection with his 1864 classification that "it ... did not escape my notice that the second table with the group Zn, Cd, Hg could be joined to the left side of the first, and thus united with it to form a whole" (ibid.). Nevertheless, at the time this classification was presented Meyer gave no sign of having noticed any such possibility of uniting the two tables.

[53]See n.31, above.

[54]Spronsen, also, recognises Meyer's 1868 system, but not his classification of 1864, as representing a periodic system (see Bibl.110, pp.125-7).

Over and above such questions of the bare achievement of independent construction of what we can recognise as prototype periodic systems, many further questions arise in connection with the contributions of de Chancourtois, Newlands, Odling, Hinrichs, Meyer and Mendeleev in the field of the periodicity of the elements - concerning the details of their particular periodic systems; the extent to which they discussed, developed and applied their systems; their assessments of the relative significance of their own and related contributions; and the degree of attention and value given to their work by the scientific community in general. Some of these further questions are in certain respects probably of greater importance than questions of bare discovery. Although concurring with Spronsen's conclusion that "we do not consider only one or two scientists (Mendeleev, Meyer) to be the discoverers of the periodic system ... We recognise six independent discoverers: Béguyer de Chancourtois, Newlands, Odling, Hinrichs, Meyer and Mendeleev",[55] I feel unable to agree with his further assessment that, "The fact that some of these scientists explained or predicted more than others by making deductions from their system is of secondary importance".[56] The most important aspect of scientific discovery would seem to be not the bare achievement of discovery inherent in the (possibly unappreciated or even unknown) work of some particular scientist or scientists (what we might call "private" discovery), but rather discovery by the scientific community ("public" discovery): more important than questions of priority of discovery in the "private" sense are questions of primacy of contribution leading to discovery in the "public" sense. Mendeleev (for whom we shall be claiming such primacy in connection with the discovery of the periodic law) himself expressed a view close to this: "he who should justly be considered creator of a scientific idea is he who has understood not only the philosophical but also the practical aspect of the matter, who has known how to present it such that all can be convinced of the new truth and it has become common property. Only then is the idea ... not lost" (1880).[57] In the history of the periodic law it was the use of

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[55] Bibl.110, pp.142-3.

[56] Ibid., p.143.

[57] Zur Geschichte des periodischen Gesetzes, Berichte, 13 (1880) 1796-1804; p.1802 (PLBA, 404).

the periodic system as a basis for explanation and prediction (largely by Mendeleev) which more than anything led to its "public" discovery, and which, contrary to Spronsen's assessment, would therefore seem to be of primary importance.

Each of the six independent compilers of prototype periodic systems discussed to some extent the structure and significance of his system(s). In de Chancourtois' discussion of his vis tellurique the periodicity illustrated therein was given no special prominence, being acknowledged only as one of a variety of relationships manifested in this system. Hinrichs also had little to say about the rudimentary periodicity manifested in his systems, being much more concerned with ideas of the composition of chemical atoms from the ultimate atoms ("panatoms") of primary matter ("pantogen"), ideas which he did not relate to any significant extent to the periodicity of the elements. The publications of Newlands (1864-6), Odling (1864-5), Mendeleev (1869-71) and Lothar Meyer (1870) on the other hand show a definite and predominant recognition of, and concern with, the periodicity of the elements, although perhaps less explicitly so in Odling's case. Newlands, Mendeleev and Meyer all gave succinct verbal statements of that regularity of recurrence of properties which is illustrated in their classificatory systems, as also did de Chancourtois (in a less prominent manner): thus -

i) de Chancourtois (in the "complement" to his "fundamental theorem"): "Each helix drawn through two characteristic points [sc. points corresponding to particular atomic-weight values on the surface of de Chancourtois' cylinder] and passing through several other points or only near them, brings out relations of a certain kind between their properties; likenesses and differences being manifested by a certain numerical order in their succession, for example, immediate sequence or alternation at various periods" (1862);[58]

ii) Newlands ("law of octaves"): expressed variously, e.g. "the eighth element starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music" (1864);[59]

iii) Mendeleev ("law of periodicity" or "periodic law"): expressed variously, e.g. "The elements, arranged according to the magnitude of their atomic weights, present a clear periodicity of properties" (1869);[60]

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[58] See Ch.III, p.132. My underlining.

[59] See Ch.III, p.137.

[60] See Ch.III, pp.163 and 167.

iv) Lothar Meyer: "the properties of the elements are largely periodic functions of the atomic weight" (1870).[61]

The only possibly comparable comments made by Hinrichs were certain expressions of unspecified lawlike correlation between the properties of the elements and their atomic weights, e.g. "The properties of the chemical elements are functions of their atomic weights" (1867)[62] (cf. the similarly general comment by de Chancourtois, 1863 - "The properties of bodies are the properties of numbers"[63] - and that by Mendeleev, 1869 - "the magnitude of the atomic weight determines the nature of an element"[64]). Odling in discussing his classificatory systems gave neither a succinct verbal statement of periodicity like de Chancourtois, Newlands, Mendeleev and Meyer, nor even an expression of unspecified correlation like Hinrichs. He did, however, write in reference to the table presented by him in 1865 in Watts' Dictionary of Chemistry (see Fig. III-7), "Doubtless some of the arithmetical relations exemplified in the foregoing table are merely accidental, but, taken altogether, they are too numerous and decided not to depend upon some hitherto unrecognised general law"[65]; in an almost identical comment in his article On the proportional numbers of the elements, 1864, Odling had referred to "the foregoing tables and remarks" rather than to "the foregoing table".[66]

Many years after this explicit rejection by Odling of the possibility that all of the regularities manifested in his classificatory systems of 1864-5 could be dismissed as being merely "accidental", Mendeleev (1902) was to remark similarly that the periodicity of the elements "could not possibly be taken to be the result of chance".[67] Such an attitude had indeed been implicit in Mendeleev's comments from the very beginning of his work on the periodic law, as it had been also in the comments of de Chancourtois, Newlands and Lothar Meyer. Hinrichs probably held a similar view, although

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[61] See Ch.III, p.152.

[62] See Ch.III, p.151.

[63] See Ch.III, p.133.

[64] See Ch.III, p.163.

[65] Bibl.129, vol.III, 1865, p.976.

[66] See Ch.III, p.145.

[67] See Ch.V, nn.36 and 37.

there is perhaps a slight doubt about this.[68] None of the six discoverers of the periodic system proposed any specific hypothesis about the cause of the periodicity of the elements, but they all (with the possible, though unlikely, exception of Odling) were attracted to some extent towards the idea of the complexity of the elements,[69] and in a vague sense undoubtedly felt that a connection exists between the particular structural nature of the elements and the periodicity of their properties: this was certainly true for de Chancourtois, Lothar Meyer and Mendeleev, and seems to have been so also for Newlands.[70]

Although all six discoverers of the periodic system seem to have recognised the existence of certain analogies between the chemical elements and compound radicals, and were (with the possible exception of Odling - see above) inclined to take this as evidence that the chemical elements may themselves be complex, only de Chancourtois included also compound radicals

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[68] Venable (Bibl.124, p.89) has written: " Hinrichs states in a later publication that it [sc. his Atomechanik] contains, explicitly stated, all that is true in the periodic law. He is a vigorous critic and opponent of this law, however, and may mean by this statement that he regards very little of it as true". Venable gives no source-references here, and I have been unable to discover just in what sense Hinrichs became 'a vigorous critic and opponent" of the periodic law. In presenting his classificatory systems of 1867-9 Hinrichs does not appear to have related in any significant way the fairly regular recurrence of properties shown by the elements in these systems to his strongly-held views on primary matter, which suggests that at the time he did not think this pattern of recurrence of properties to be of any great importance. Afterwards, he may, just possibly, even have gone to the extreme of considering the periodicity of the elements as being merely fortuitous.

[69] I have come across no reference by Odling to the idea of a complexity of the chemical elements, although his adherence in 1863 to a Proutian-type commensurability hypothesis (see Ch.II, p.64) suggests that he probably did not consider the elements to be qualitatively-distinct entities.

[70] Mendeleev's views on the ideas of primary matter and the complexity of the elements, and on the significance of the periodic law for such ideas, are discussed in Ch.II; his considerations on the question of the cause of the periodicity of the elements are presented in Ch.V.

Various comments by Newlands on the subject of the complexity of the elements are to be found in the Appendix to Bibl.84, 1884.

(Regarding Hinrichs' attitude, see n.68 above).

together with the elements in his classificatory system. This quite probably tended to lessen the value of de Chancourtois' system in the eyes of those (relatively few) chemists of the time who were aware of his work; and from the standpoint of present-day chemistry we can see the inclusion of compound radicals as a feature of the vis tellurique which makes it a lesser development towards the modern periodic system than were the systems of Newlands, Odling, Hinrichs, Meyer and Mendeleev. It should be recognised, however, that the classification of certain compound radicals together with the elements was not unnatural in the context of de Chancourtois' ideas on the question of the decomposability of the elements: de Chancourtois believed - in accordance with his view that "the properties of the elements are the properties of numbers"[71] - that "bodies which are really simple, or at least irreducible by the ordinary means at our disposal" are not the commonly-recognised chemical elements as a whole, but only those elements whose atomic weights correspond to prime numbers[72]; between the elements whose atomic weights are not prime numbers, and stable compound radicals such as NH_4 and CN, no essential difference seems to have been recognised by de Chancourtois.

The periodic classificatory systems of de Chancourtois, Newlands, Odling, Hinrichs, Meyer and Mendeleev all demonstrate a concordance between arrangement of the elements according to increasing atomic-weight value on the one hand, and according to family-resemblance (chemical analogy) on the other. As Odling wrote in presenting his first periodic classification in 1864, "With what ease this purely arithmetical seriation [sc. of the elements according to increasing atomic weight] may be made to accord with a horizontal arrangement of the elements according to their usually received groupings, is shown in the following table [sc. the table presented in Fig. III-6]";[73] and Mendeleev in 1871 made the similar point that "in the form of the oxides and in the atomic weights of the elements" we find two "stable numerical guiding principles for the distribution of the elements" according to the periodic law.[74] But within this common general pattern of classification the particular significance of atomic weight was not always the same. In de Chancourtois' vis tellurique the positions of the elements

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[71] See Ch.III, p.133.

[72] See Ch.III, p.132.

[73] Bibl.85, p.643.

[74] The periodic lawfulness of the chemical elements (G.), Annalen, 1871, p.164 (PLBA, 126).

reflect the actual magnitudes of the atomic-weight values: not only are the elements arranged in the order of increasing atomic weight, but also the spacing between the elements reflects the actual magnitude of the atomic-weight differences.[75] In the tabular periodic systems drawn up by Newlands, Odling, Meyer, Hinrichs and Mendeleev, however, where the elements are arranged in rows and columns in which the available places are regularly spaced, the significance of atomic weight is retained only in the principle of atomic-weight ordering, there being no reflection beyond the ordinal position of an element of the precise magnitude of its atomic weight. Insofar as these tabular systems, unlike de Chancourtois' vis tellurique (or Lothar Meyer's "atomic-volume" curve), tend to embody an oven-spaced ordering of elements rather than reflect the precise numerical value of atomic weight, we can already see in them a germ of the subsequent idea of "atomic number", in the sense of the latter as the ordinal number of the position of an element in the periodic table.[76] (A somewhat different type of anticipation of atomic number, in the sense of the latter as the characteristic ordinal number of an element, may be seen in Newlands' explicit assigning of ordinal numbers to the elements on the basis of

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[75] Lothar Meyer's "atomic-volume" curve of 1870 (see Fig.III-15) is like de Chancourtois' vis tellurique in this respect. However, Meyer's curve is not really a periodic system, illustrating the common pattern of periodicity of many properties, but rather an exact representation of the periodicity shown by one particular numerical property (viz. "atomic volume").

[76] The actual order of the elements tellurium and iodine in these early tabular periodic systems in fact corresponds to the order of atomic number (in the modern sense) rather than to the order of atomic-weight values, despite the order-by-atomic-weight basis of the tables. The compilers of these early periodic tables tend to have believed (mistakenly) that this instance of atomic-weight inversion, which was demanded on grounds of chemical analogy (of Te with O, S and Te, and of I with F, Cl and Br), would disappear with a subsequent re-determination of the atomic weight of tellurium or iodine (or both).

Although in some of the periodic tables of 1864-71 (e.g. in Lothar Meyer's 1868 manuscript table, Fig.III-13, and in Mendeleev's tables 15, 30-33, 35 and 36) cobalt and nickel were similarly included in the order of atomic number, in what we can now recognise as inverted atomic-weight order, unlike the case of iodine and tellurium this atomic-weight inversion was not recognised at the time because Co and Ni were taken to have the same atomic-weight value (see Ch.VI, p.348).

position in the series of elements arranged according to increasing atomic weight[77]).

The significance of the actual atomic-weight values of the elements had thus become somewhat diminished in the tabular periodic systems of Newlands, Odling, Hinrichs, Meyer and Mendeleev as compared with the vis tellurique of de Chancourtois and the majority of the attempts which had been made at classifying the elements during the 1850's. However, Odling, Hinrichs, Meyer and Mendeleev appear not to have fully appreciated this diminution of significance of the actual atomic-weight values which was implicit in their periodic tables. All four continued to pay great attention to actual values of atomic weights and atomic-weight differences.[78] Only Newlands - in explicitly assigning ordinal numbers to the elements according to their position in the series of increasing atomic weights - seems to have recognised that the significance of atomic weight for the periodic classification of the elements does not lie directly in the actual numerical

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[77]Since Newlands' ordinal numbers were assigned strictly according to the currently-accepted atomic-weight values, and since his tables illustrating the "law of octaves" had certain inversions in the order of the elements with respect to these atomic-weight values (e.g. for Te and I), his ordinal numbers do not coincide exactly with the order of the positions of the elements in his tables (see Figs. III-3, III-4 and III-5). It is for this reason that Newlands' ordinal numbers represent a somewhat different type of anticipation of the modern atomic number from that implicit in the tendency for even-spaced ordering of the elements in his and other early tabular periodic systems.

A significant difference between the system of modern atomic numbers and Newlands' system of ordinal numbers is to be seen in the fact that in certain cases Newlands assigned the same ordinal number to two elements (see Figs. III-4 and III-5).

[78]Mendeleev's concern with atomic-weight values and differences is perhaps best seen in his long article of 1871 in Liebig's Annalen (see, for example, Ch.V of the present thesis, pp. 296-7, and n.73 on p.312). Although Mendeleev later strongly emphasised the discrete nature of the dependence shown in the periodic law, criticising representations of this periodicity which employed continuous functions or curves (see Ch.V, pp.293, 297-9), his concern with actual atomic-weight values and differences still did not appear to diminish to any appreciable extent.

atomic-weight values.[79]

With the possible exception of Hinrichs, all six discoverers of the periodic system seem to have believed in the strict validity of the principle of atomic-weight ordering in their systems: although Hinrichs wrote in presenting his two periodic tables of 1869 that the elements in these tables are arranged according to increasing atomic weight,[80] the central region of both tables in fact contains certain series of elements in the order of decreasing atomic weight (see Figs. III-10 and III-11), with no indication that such an arrangement was considered in any way unsatisfactory or provisional. All six discoverers adhered to the (less precise) principle of family-resemblance in their periodic systems.[81] Two further principles which tended to be followed in the construction of the tabular systems, with their relatively clearly-defined places, were those of the "non-zero-occupancy" of places and the "non-multiple-occupancy" of places, i.e. those of the filling of vacant places which were indicated in

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[79]The conclusions arrived at here concerning the significance of atomic weight for the early periodic classifications are essentially the same as those which have already been presented by F.A. Paneth (see Bibl.90). Paneth has written, for example, that "the limited significance of the atomic weights has in a sense been implicit in any table of the periodic system, because here - in contradistinction to its representation by curves - the elements were always arranged at equal distances from each other and not according to the actual values of the atomic weights. The first scientist who drew the consequences from this fact was the Swedish physicist Rydberg who, in a paper of 1897, stated with admirable clarity: 'In investigations on the periodic system not the atomic weights, but the ordinal numbers of the elements, have to be used as independent variables'. Decisive progress in the understanding of the periodic system could only be made when chemists had freed themselves from their overestimation of the theoretical consequence of atomic weights" (Paneth, op.cit., pp.33-4; J.R. Rydberg, Zeitschr.anorg. Chem., 14, p.94). In discussing Newlands' "law of octaves" and the classificatory tables based upon it, Paneth felt that Newlands "had been guided by a remarkably sure instinct" in giving prominence to his ordinal numbers rather than to the actual atomic-weight values (op.cit., p.44).

[80]The Pharmacist (Chicago College of Pharmacy), 2 (July 1869) 10-12; Proc.Amer.Assoc.Adv.Sci., 18 (1869) 112-124.

[81]Only Mendeleev of the six discoverers felt that he had established a generally reliable criterion of family-resemblance, viz. maximum valency in "saline" oxides, corresponding to group-number in the periodic table (see pp.185-9 and 308-11).

the system and the restriction of just one element to each place.[82] The latter requirement, of the non-multiple-occupancy of places, was not always rigidly adhered to: thus, Newlands was quite prepared to allow double-occupancy of certain places in his tables of 1865-6[83]; Mendeleev allowed triple-occupancy or even quadruple-occupancy of places in group VIII of his short-form periodic table[84]; and Hinrichs' tables of 1869 had multiple-occupancy of one of the places.[85] The requirement of non-zero-occupancy of places in the periodic table provided scope not only for the inclusion of known elements which had yet to find a place, but also for the prediction of undiscovered elements. The most extensive, the most detailed, the most confident and the most successful use of the periodic table for predicting the existence and properties of unknown elements is to be seen in the work of Mendeleev[86]; of the other four independent compilers of tabular periodic

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[82]Although the arrangement of elements on de Chancourtois' vis tellurique, unlike in the tabular periodic systems, corresponds directly to the actual magnitudes of the atomic weights, the possible "places" (de Chancourtois' "characteristic points") which could be occupied did not extend over the entire range of real numbers between the lowest and highest "characteristic numbers" in the system: de Chancourtois' adherence to the Proutian commensurability hypothesis PCH (1; H=1) (see Ch.II, pp.63-4) restricted the possible "places" to those corresponding to integral values of the "characteristic numbers" (i.e. of the atomic weights, in the case of the elements; chlorine, for example, was assigned a "characteristic number" of 35 by de Chancourtois, not 35.5). There is no indication that de Chancourtois considered every integral value within the limits of the system to correspond to the place of an element. He seems not to have accepted more than single-occupancy of "places" by elements on his vis tellurique; in certain cases, however, we do find the same place occupied both by an element and a compound radical, e.g. Si and ammonium were both assigned the "characteristic number" 36.

[83]See Figs. III-4 and III-5.

[84]The places in group VIII of Mendeleev's short-form periodic tables can be seen as being quadruple-occupied if we count not only the elements of the iron, palladium and platinum families but also the coinage metals Cu, Ag and Au.

[85]The elements "Cr, Mn, Fe, Ni, Co - Ur" constitute "varieties" occupying a single place in the aluminium group in Hinrichs' table of July 1869 (see Fig. III-10, and n.157 in Ch.III); the elements "Cr, Mn, Fe, Ni, Co" occupy the corresponding place in Hinrichs' later table of 1869 (see Fig. III-11).

[86]See Ch.VI, section C.

systems (Newlands, Odling, Hinrichs and Meyer), Hinrichs showed the least tendency to make predictions concerning unknown elements. The placing of known elements in the periodic systems of 1862-71 on the basis of the requirements of atomic-weight ordering, family resemblance and (where demanded) single-occupancy of places supported and consolidated many of the existing atomic-weight determinations and assessments of family-membership which had hitherto been the subject of (often appreciable) doubt: this was especially the case for some of the lightest elements (Mendeleev's "typical" elements[87]), which tend to show certain peculiar properties and less clearly-defined family-resemblances than the heavier elements. Where there appeared to be a discrepancy in the indications of the principles of atomic-weight ordering, family-resemblance and (where demanded) single-occupancy for the placing of a particular element in the periodic system there was a tendency to attribute this to an error in the assumed atomic-weight value, or to an incorrect assessment of family-membership, or perhaps to both, of one or more of the elements involved. This tendency is to be found to some extent in the work of all six discoverers of the periodic system, although appreciably less so for de Chancourtois and Hinrichs than for Newlands, Odling, Meyer and Mendeleev.[88] In de Chancourtois' case this may have been partly a consequence of the greater complexity of the pattern of relationships with which he was concerned in connection with his system, as compared with the predominant concern shown by Newlands, Odling, Meyer and Mendeleev with the "periodic" relationship; in Hinrichs' case it possibly reflects a lesser estimation on his part of the significance of the periodic system. Sometimes the atomic-weight value or family-membership (or both) was actually changed so as to remove the discrepancy - even solely on the basis of the theoretical demands of the classificatory system, without any empirical support (it was assumed in such cases that the latter would eventually be forthcoming). Many of the changes which were thus felt to be necessary, and sometimes even actually adopted, were in fact vindicated by subsequent empirical results or according to the present-day interpretation of the structure of the periodic system (e.g. Mendeleev's doubling of the atomic weight of uranium to 240; and the reassessment by Odling, Newlands, Mendeleev and Meyer of family-membership for thallium); others were not, notable among these being the adoption or expectation of a higher atomic

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[87] Concerning Mendeleev's designation of the lightest elements as "typical", see Ch.III, n.205.

[88] Concerning Mendeleev's tendencies in this direction, see Ch.VI, sections A and B.

weight for iodine than for tellurium, in accordance with the placing of Te before I in the periodic system on the basis of the demands of family-resemblance. Various specific instances of the use of the early periodic systems for assessing family-membership and atomic-weight values, and for predicting unknown elements, are reviewed below.

In de Chancourtois' vis tellurique (1862) the closest family-resemblance indicated for hydrogen appears to be with zinc. Odling classified hydrogen with Ag and Au in 1864, and with Au but not Ag in one of his 1865 tables (Fig.III-8).[89] Newlands in 1865-6 listed hydrogen in the same group as the halogens, as did Hinrichs in 1867; in Hinrichs' tables of 1869 hydrogen was placed in a group of its own. Lothar Meyer did not include hydrogen in his classificatory systems of 1864, 1868 and 1870[90] (in 1872 he included H in the same column as Ni, Pd and Pt). Between 1869 and late 1870 Mendeleev classified H in various ways (see Fig. III-18) - on its own, with the coinage metals, with the iron-family elements (cf. Meyer 1872), eventually including it in group I in the same sub-group as Na, Cu, Ag and Au, a placing which he retained for it in all of his subsequent tables. Mendeleev appears never to have included hydrogen in the halogen group.

During the 1850's the three elements C, B and Si had commonly been taken to be members of the same natural family, sometimes within a larger family which included also one or more of the elements Ti, Zr and Sn.[91] In the periodic systems of 1862-71 boron was no longer included in this family. De Chancourtois classified B (11) as an analogue of Al (27)[92], as did Odling in 1864, Newlands by 1865, Mendeleev in his "attempt at a system", 1869, and Meyer by 1870. Meyer had been unable to place B and Al in his 1864 classification; in 1868 he still omitted B, and included Al only unsatisfactorily (see Fig. III-13). Since he had seen Mendeleev's "attempt at a system" before constructing his own system of 1870, it is very likely

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[89] Concerning Odling's re-positioning of Au in 1865, see below.

[90] Hydrogen was included in Meyer's "atomic-volume" curve of 1870, but this curve is not really a classificatory system (see n.75 above).

[91] See Ch.III, section B.

[92] On the basis of the manifestations of isomorphism among the feldspars and pyroxenes, de Chancourtois in 1863 suggested the adoption of a doubled atomic-weight value of 55 (= 7 + 3 x 16) for Al - presumably as a "secondary characteristic" rather than as the only "numerical characteristic" for Al - in order to bring this element onto the same generator as Na (23 = 7 + 16) and K (39 = 7 + 2 x 16), two elements with which it is associated in these minerals: "this would render perfect the parallelism between the elements of the feldspars and the pyroxenes" (Comptes rendus, 56, p.479; see Bibl.26, p.188).

that Meyer was aided in his placing of B and Al in 1870 by this knowledge of Mendeleev's work. Hinrichs did not include boron in his circular system of 1867, or in his table of the autumn of 1869; in his table of July 1869 he included boron in a separate group between the aluminium and carbon groups, with Mo and W as higher analogues.

Although the magnesia-type formula had been proposed for beryllium oxide as early as 1842 (by Avdeev), many chemists in the 1860's still favoured Berzelius' alumina-type formula for this compound, which gave beryllium an atomic weight of ca. 14 rather than ca. 9. However, the requirements of their classificatory systems led de Chancourtois (1862), Meyer (as early as 1864), Newlands and Odling (by 1865) and Mendeleev (in his first periodic system, 1869) to list Be with an atomic weight of ca. 9 as an analogue of magnesium: no place (either vacant or already occupied) exists in these systems for a trivalent element of atomic weight ca. 14 with the properties of beryllium, whereas divalent beryllium of atomic weight ca. 9 fits reasonably well into the system as a lower analogue of magnesium. Unlike the other five discoverers of the periodic system, Hinrichs had difficulty in placing Be. He seems to have given it the correct atomic weight of ca. 9 (rather than ca. 14), but could not decide between placing it with Mg or with Al (see particularly Fig.III-10). It was not until the mid-1880's that the indication of the periodic system regarding the atomic weight of beryllium finally came to gain overwhelming acceptance.[93]

Irregularities of atomic-weight ordering among the heaviest elements constituted a prominent feature of many of the early periodic systems, these irregularities being a consequence partly of the incorrect atomic-weight values assigned to Os, Ir and Pt at the time, and partly of the particular family-resemblances which had been assessed for such elements as Au, Hg, Tl and Pb.[94] Meyer (1870) and Mendeleev (1870-1) felt that future atomic-weight determinations would indicate somewhat lower values for the elements of the

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[93] A brief general survey of the problem of the atomic weight of beryllium, together with an account of Mendeleev's involvement with this problem, is given in Ch.VI, section B. Concerning Newlands' reaction to the problem in the light of his "law of octaves", see his recollections of 1884, Bibl.84, p.viii.

[94] Thallium had been discovered in 1861, and had not yet been extensively characterised. (Of the other three elements which had been discovered in the early 1860's - Cs in 1860, Rb in 1861, In in 1863 - caesium and rubidium posed no problem for the periodic system, being included as higher analogues of potassium. The problem of indium is considered below).

platinum family[95], an expectation which was indeed confirmed during the course of the 1870's and 1880's. As for the irregularities associated with the initial placings of Au, Hg, Tl and Pb, a reassessment of principal family-resemblance for one or more of these elements, resulting in adjustment of family-membership without change of atomic-weight value, was made by Odling (1865), Newlands (1866), Mendeleev (1869) and Meyer (1870) in an attempt to remove these irregularities[96], e.g. all four of these scientists moved Tl from the alkali-metal group to the aluminium group. All but one of these changes were in the direction of increasing correspondence with the modern periodic table; the exception was Odling's re-positioning of Au in 1865, this element having been correctly placed (i.e. in its present-day position) in his 1864 table. This re-positioning of Au by Odling was clearly induced by the desire to remove the irregularity of having Au placed after the platinum elements, which at the time were assigned atomic weights greater than that of Au.

All six discoverers of the periodic system except for de Chancourtois placed Te and I in their systems in inverted atomic-weight order in accordance with the demands of family-resemblance, and seem to have believed that a future re-determination of the atomic weight of one or both of these elements would probably remove this anomaly. Newlands, for example, writing some time after the era of discovery of the periodic system,[97] remarked, "Tellurium ... I have always placed above iodine, from a conviction that its atomic weight may ultimately prove to be less than that of iodine" (1884)[98]. Only Mendeleev of the discoverers actually went so far as to assign a new atomic-weight value solely on the basis of this placing of Te before I, taking Te = 125 instead of 128 (with I = 127).[99] It is interesting to note that although de Chancourtois placed I (127) before Te (128) on his vis tellurique, he ascribed atomic-weight values of 79 and 80 to Br and Se respectively, which had the same effect of bringing Br into alignment with I, and Se with Te; and since the currently-accepted equivalents for Br and

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[95] Meyer, Bibl.81 (see Bibl.67, p.16). For Mendeleev's discussion of the question, see Ch.VI, pp. 347-8.

[96] Concerning Mendeleev's contribution, see pp.193 (Fig.III-19) and 325. Newlands' contributions in this direction were later summarised by him in Bibl.84 (1884), p.viii.

[97] In the present thesis the "era of discovery" of the periodic system is taken as being 1862-71 (see p.109).

[98] Bibl.84, p.viii.

[99] The history of Mendeleev's views concerning the atomic weights of tellurium and iodine is considered in Ch.VI, pp.343-7.

Se gave the atomic-weight values the other way around (i.e. Br = 80, Se = 79), it seems likely that de Chancourtois altered these values specifically for reasons of family-resemblance in his system. Whereas in the periodic systems of Newlands, Odling, Hinrichs, Meyer and Mendeleev inversion of Br and Se instead of Te and I would have created clear problems in connection with alignment of these elements with their lighter analogues, in de Chancourtois' system - reflecting as it did the actual numerical values of the atomic weights and atomic-weight differences - the inversion of Br and Se probably seemed preferable (since it brought the elements O, S, Se and Te into exact alignment; inversion of I and Te, on the other hand, would have given exact alignment for neither the halogen family as a whole nor the oxygen family).

Indium was not included in de Chancourtois' vis tellurique (it was discovered only in 1863, after the construction of this system), or in any of Odling's tables of 1864-5. Newlands included it in his tables of 1865-6, in the C - Si group, assuming for it an atomic weight of 72.[100] Hinrichs included it in his 1867 system with an "atogram" of 142 (corresponding to an atomic weight of 71), in the same group as Li, Cs and Tl, but omitted it from his tables of 1869. Meyer omitted it from his tables of 1864 and 1868. Mendeleev could not fit it (as In = 75) into his "attempt at a system", 1869, and suggested as a result that its assumed atomic-weight value could well be wrong; but it was not until the summer-early autumn of 1870 that Mendeleev came to assign the new atomic-weight value of ca. 113 to In, placing this element in his periodic system as an analogue of B and Al.[101] By this time, however, Lothar Meyer had already published (in March, 1870) a periodic table with In = 113.4 included as an analogue of Al. Although Mendeleev had seen Meyer's paper of March 1870 very soon after its publication,[102] he did not acknowledge Meyer's modification of the atomic weight of indium when he himself subsequently adopted the same modification later in the year. Specific-heat measurements on metallic indium by Bunsen and (independently)

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[100] See, for example, On the cause of numerical relations among the equivalents, Chem. News, 12 (1865) 94. Earlier, in 1864, Newlands had assumed an atomic weight of 74.14 for indium (see Ch.III, n.120). In 1884 Newlands claimed in reference to his work of the 1860's on the "law of octaves" that "I have applied the periodic law to ... Predicting the atomic weight of an element whose atomic weight was then unknown, viz. that of indium" (Bibl.84, p.vii); what he does not also point out, however, is that this prediction had already been shown to be false long before 1884.

[101] See Ch.VI, pp.335-41.

[102] This is indicated by a reference made by Mendeleev to Meyer's paper in the spring of 1870 (see Ch.III, p.171).

by Mendeleev during the autumn of 1870 supported the atomic-weight value of ca. 113 for indium. The modern periodic system has retained the placing and atomic-weight value given to indium by Meyer and Mendeleev in 1870.

Adopting the atomic-weight value of 120 given by Cannizzaro for uranium, Odling (1864) and Newlands (1865-6) included this element in their periodic systems as an analogue of aluminium. However, this led to the irregular atomic-weight ordering Cd = 112, U = 120, Sn = 118, Sb = 122. Odling's reaction to this problem was to omit uranium from his tables of 1865; the initial reaction of Mendeleev on the other hand (in his "attempt at a system", March 1869) was to include uranium as an analogue of aluminium, in the place between Cd and Sn, and to alter its atomic-weight value to 116 to accord with the principle of atomic-weight ordering.[103] By mid-1869, however, Mendeleev's work on the atomic volumes of the elements had led him to remove uranium from the place between Cd and Sn; and while he temporarily re-adopted Cannizzaro's value of U = 120 for want of an alternative value, he now felt that a more drastic revision of the atomic-weight value of this element was needed. Early in 1870 Mendeleev proposed the value U = 240 (publ. March, 1870), with uranium now seen as an analogue of chromium. By the end of 1869 Lothar Meyer also had come to feel that the atomic-weight value U = 120 should be changed, suggesting the new value U = 180 in his article published in March 1870 (written December 1869). At the same time Meyer thought that perhaps the currently-accepted atomic-weight value of ca. 92 for cerium should also be changed, although he did not suggest an alternative value in this case. In the summer-early autumn Mendeleev came to propose the value of ca. 140 for the atomic weight of cerium, placing this element in group IV of the periodic system as a higher analogue of Ti and Zr. Before this time he had given no definite indication of having doubted the value Ce = 92.[104]

We see, therefore, that when Mendeleev wrote in 1871, "At the same time as Mr. Meyer I had come to the idea of proposing a change in the atomic weights of In, Ce and U",[105] he was being fair neither to himself nor to Meyer. The actual, rather complicated story seems to have been as follows: Mendeleev appears to have been the first to recognise the need for a change

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[103] An account of the history of Mendeleev's adjustment of the atomic-weight value for uranium is given in Ch.VI, pp. 332-5.

[104] However, the very fact that he had been unable to place Ce = 92 satisfactorily in his original "attempt at a system", 1869, had quite possibly already suggested to Mendeleev that this atomic-weight value should be changed.

[105] Zur Frage über das System der Elemente, Berichte, 4 (1871) 348-52; p.351 (PLBA, 389-90).

in the atomic weights of indium and uranium in the light of the periodic law, the first to suggest the correct value for uranium (viz. 240), and the first to suggest a definite value for the modified atomic weight of cerium (viz. ca. 140, the correct value[106]); Lothar Meyer, on the other hand, appears to have been first to propose the need for a change in the accepted atomic-weight value of cerium, and the first to make a definite suggestion as regards a modified value for indium (viz. 113.4, the correct value). Lothar Meyer's proposals of atomic-weight modification on the basis of the periodic system were presented by him with a strong note of caution: "It would be rash to change the accepted atomic weights on the basis of so uncertain a starting-point".[107] Mendeleev was much bolder than Meyer in this respect.

Atomic-weight modifications were made by Mendeleev also for the elements Y, La, Di, Er, Th (all during the summer-early autumn of 1870) and Ti (late 1870-early 1871);[108] later he came to think that future atomic-weight determinations would probably indicate a higher atomic weight for Ni than for Co, and for K than for Ar, following the pattern of his expectation for the atomic weights of tellurium and iodine.[109] The modifications proposed by Mendeleev for the former series of elements have turned out to be predominantly correct[110]; his expectations concerning Co - Ni and Ar - K, as in the case of Te - I, have, on the other hand, not been confirmed. Long before Mendeleev came to adopt the (correct) atomic-weight value of ca. 232 for thorium, similar values had already been assumed for this element by Newlands and Odling in 1864[111]; also, the (correct) atomic-weight value of 48 (rather than 50) which Mendeleev adopted for titanium had already been assumed much earlier by Meyer (1864) and Odling (1865).[112]

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[106] Although Mendeleev assigned the correct atomic-weight value of ca.140 to cerium, his consequent placing of this element in the periodic system as an analogue of Ti and Zr in group IV does not correspond to its present-day placing.

[107] Bibl.81 (see Bibl.67, p.17).

[108] See Ch.VI, sub-section B-1.

[109] See Ch.VI, sub-section B-2.

[110] As regards the case of titanium, the confirmation of Mendeleev's atomic-weight modification (from 50 to 48) can be seen as little more than a fortuitous success of his use of the periodic system (see p.327).

[111] Newlands: Th = 238 (see, for example, Chem.News, 10, July 1864, p.59). Odling: Th = 231.5 (Fig.III-6), Th = 231 (Fig. III-7).

[112] See Fig.III-12 (Meyer), Figs. III-7 and III-8 (Odling).

De Chancourtois does not appear to have made any predictions concerning undiscovered elements on the basis of his vis tellurique.[113] Newlands, in his "pre-periodic" classificatory work of 1863, made a number of predictions concerning the existence and atomic-weight values of supposed missing elements, e.g. a missing alkali metal of atomic weight 163 was predicted;[114] but these predictions, being based upon pre-Cannizzaro "atomic-weight" values, and different kinds of "atomic-weight" relationship within the different chemical families, have little significance as anticipations of elements which have since been discovered. In his first "periodic" classificatory system (based upon Cannizzaro's atomic weights), July 1864, Newlands left a gap in the C - Si - Sn group between Si and Sn for a missing element whose atomic weight he predicted as 73;[115] this prediction represents an anticipation of the element germanium (discovered 1866), and came more than five years before Mendeleev's corresponding prediction of "eka-silicon". In his tables of 1865-6 Newlands no longer left gaps for possible new elements; in 1866 he was criticised for this by Gladstone.[116] Odling considered it probable that new elements would be discovered corresponding to some or all of the vacant places marked in his periodic tables of 1864-5; in 1864 he listed as a lower analogue of Ag and Au an element "X 63" (apparently distinct from copper, which he placed elsewhere in the system as "Cu 63.5")[117]. Although Hinrichs appears to have said nothing about the possibility of undiscovered elements, it is quite likely that he considered that the vacant places marked in his tables of 1869 might represent such elements. Lothar Meyer in 1864, and also in his manuscript table of 1868, included an empty place between Si and Sn (corresponding to the place of the unknown Ge, cf. Newlands and Mendeleev), which he did not remark upon but which he probably considered to represent a possible missing element. Meyer's periodic table of 1870 had various gaps, but again no accompanying suggestion that these might correspond to undiscovered elements. Mendeleev, from the beginning of his work on the periodic law (March 1869), used the periodic system extensively as a basis for the prediction of the

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[113] On the question of what constituted possible "places" in de Chancourtois' system, see n.82, above.

[114] See Ch.III, p.134.

[115] See Ch.III, p.134.

[116] See Ch.III, pp.138-9.

[117] See Ch.III, p.141.

existence and properties of unknown elements.[118] Mendeleev's predictions concerning missing elements varied greatly in detail, and in the degree of confidence with which they were made. Generally speaking, Mendeleev was much more confident in his predictions based upon interpolation of the periodic system than in those based upon extrapolation of the system,[119] and more confident in his earlier predictions than in his later predictions.[120] The most detailed series of all of his predictions, and also the most confidently made, were those of 1870-1 involving "eka-boron" (= scandium, discovered 1879), "eka-aluminium" (= gallium, discovered 1875) and "eka-silicon" (= germanium, discovered 1886); these predictions were convincingly confirmed in all but a few respects.[121] The most detailed series of false predictions made by Mendeleev involved either his erroneous assumption for the atomic-weight region between Ba and Ta of the pattern of periodicity shown elsewhere in the system (particularly his predictions for "eka-cadmium", made with moderate and seemingly diminishing confidence from 1889 onwards), or else his extrapolation at the edge of the system (particularly the tentative conjectures presented by him in the early 20th century in connection with his "chemical conception" of the luminiferous world-ether).[122] It should perhaps be emphasised that Mendeleev's use of the periodic system for prediction of missing elements and their properties, as also for atomic-weight modification, did not in itself constitute an activity of a novel kind: related activities can be recognised as far back as the work of Döbereiner. But the scale and detail of Mendeleev's contributions in this direction was something quite unprecedented; moreover, it was directly as a result of the striking degree of confirmation of the most detailed of Mendeleev's predictions - viz. those concerning "eka-boron", "eka-aluminium" and "eka-silicon" - that the periodic law came to gain widespread attention and appreciation.

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[118] See Ch.VI, section C.

[119] See, for example, his comment of 1870-1 quoted on p.370.

[120] It is not really surprising that the predictions which seemed the most likely to be correct should have been made first.

[121] See Ch.VI, pp.353-68.

[122] See Ch.VI, pp.396-8 ("eka-cadmium") and 369-74 ("pre-hydrogen" elements).

The fact that family-resemblances among the elements are not always clear-cut had already been recognised during the 1850's - especially by Cooke (1854-5), in his inclusion of certain elements in more than one family group ("series"), his recognition of "affiliations of the series", and his recognition of sub-groups ("sub-series") with the family groups.[123] De Chancourtois' "fundamental theorem" and its "complement" (1862) are worded in such general terms that in principle they cover all relationships of resemblance and difference among the elements; but in practice the only particular relationships of resemblance which were clearly identified by de Chancourtois were those of closest family-resemblance, manifested along the generators of his cylinder (e.g. between Li, Na and K; F and Cl; etc.). It is not until Odling's work of 1864 that we find the first clear recognition of sub-groups within larger family groups.[124] A recognition of sub-groups is to be seen also in Hinrichs' work of 1867 (and, in a rather different sense, in the "varieties" which he includes within the aluminium group in his tables of 1869)[125], in Mendeleev's work (from March 1869[126]), and in Lothar Meyer's work (from December 1869[127]). The question of the significance of the sub-group relationship for the structure of the periodic system - the question of whether the long-form or short-form arrangement is to be preferred - was first considered by Mendeleev, in March 1869.[128] Mendeleev showed a brief initial preference for the long-form arrangement, changed his preference to the short-form arrangement by the end of 1869, and then during the 1870's finally re-established a preference for the long-form arrangement.[129] Of the other early compilers of tabular periodic systems, Newlands and Hinrichs drew up short-form tables, as did Meyer in 1870 (and 1872); Odling, and Meyer in 1868, employed long-form arrangements. In his Correlation of properties (R.), 1869, Mendeleev pointed to the "transitional" character of the elements of the iron, palladium and platinum families (and also of certain

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[123] See Ch.III, p.123.

[124] See Ch.III, p.141.

[125] See Ch.III, pp.148-51.

[126] See table 4 (M4); and Ch.III, p.166.

[127] See the zig-zag arrangement of elements within the groups in Fig.III-14 (p.155).

[128] See Ch.III, p.180.

[129] See Ch.V, pp.288-9.

neighbouring elements such as Cr, Mn, Cu, etc.) in the periodic system.[130] This was the earliest recognition of the "transitional" character of such series of elements. Mendeleev was also the first to draw direct attention to the existence of "diagonal" relationships of similarity within the periodic system, particularly those between Li and Mg, Be and Al, and B and Si.[131]

Another significant contribution by Mendeleev was his development of certain aspects of the theory of valency - notably, his recognition of a general correspondence between maximum valency in "saline" oxides and group-number in the periodic system, and his discovery of the relationship between valency with respect to oxygen and valency with respect to hydrogen (the "rule of 8", later discovered also by Abegg).[132]

The classificatory work of de Chancourtois (1862-3), Lothar Meyer (1864), Newlands (1864-6), Odling (1864-5) and Hinrichs (1866-9) had very little impact upon the scientific community of the time; and although the initial response to the contributions of Mendeleev (1869-71) and Meyer (1870)[133] was certainly somewhat greater, it was still no more than moderate in its extent and enthusiasm - as Venable (1896) has remarked, it seems that in comparison with the initial response to the publications of Mendeleev and Meyer in 1869-71 "the lecture of Dumas at Ipswich [sc. at the British Association meeting of 1851] created a much greater stir among chemists, was discussed more and led more immediately to others undertaking work along the same or similar lines".[134] It was not until after the discovery of gallium in 1875 (fulfilling Mendeleev's prediction of "eka-aluminium") that the periodic law began to gain extensive recognition and acceptance.

The poor initial impact of the early periodic systems and expressions of the periodic law which appeared in the classificatory work of the 1860's and early 1870's is probably attributable to a large extent to the nature of the general attitude of the chemists of the time, which seems to have been

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[130] See Ch.III, p.166.

[131] See Ch.V, p.324.

[132] See pp.185-9, 308-11 and 315-6. Concerning Mendeleev's criticism of certain aspects of the theory of valency, see p.36.

[133] As for Meyer's 1868 manuscript contribution, this did not come to light until many years later (see Ch.III, p.152).

[134] Bibl.124, p.96.

one of weariness and disillusionment towards the apparently fruitless study of atomic-weight relationships upon which so much time and energy had been spent during the decade following Dumas' British Association address of 1851.[135] The classificatory work of the 1860's and early 1870's tended to be seen at the time as continuing in this well-worn tradition, and consequently aroused little enthusiasm - hence, for example, the refusal of the Editor of the Journal of the Chemical Society to publish Newlands' 1866 paper on the "law of octaves".[136] The general spirit of the 1860's was not yet sufficiently attuned to the developing idea of establishing a single classificatory system embracing all of the chemical elements. There were, in addition, undoubtedly various particular factors, peculiar to the individual contributions, which also acted to hinder an immediate general awareness and appreciation of the classificatory work presented by de Chancourtois, Newlands, Odling, Hinrichs, Meyer and Mendeleev during the 1860's and early 1870's. Many possible particular factors of this kind can be recognised, especially in connection with the work of de Chancourtois, Newlands, Odling and Hinrichs; for a few such factors there actually exists direct historical evidence indicating their influence, but in most cases such evidence does not exist (a certain lack of historical evidence in this connection is indeed only to be expected from the negative nature of many of the influences postulated). The particular factors which seem most likely to have contributed towards the initial lack of recognition and acceptance of the classificatory work presented by de Chancourtois, Newlands, Odling and Hinrichs during the 1860's are as follows (including, as indicated, those few factors for which direct historical evidence of influence exists):-

a) De Chancourtois

i) According to Hartog, who translated much of de Chancourtois' work on the vis tellurique into English (Bibl. 26, 1889), de Chancourtois' style was "heavy and at times obscure".[137]

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[135] Venable, Bibl.124 (1896), has written in this connection: "the public was wearied with, and distrustful of, such speculations" (p.8), "chemists had become tired of the endless symmetries and regularities offered without explanation and without use" (p.63).

[136] See Ch.III, n.127.

[137] Bibl.26, p.188. In a letter to Mendeleev dated 30th December 1889, with which he sent a copy of Bibl.26, Hartog remarked that de Chancourtois' work had been neglected "à cause de l'obscurité dans le style, et de la bizarrerie dans les idées qui caractérise cet auteur (because of the obscurity of this author's style, and the bizarre nature of his ideas)" (MALU, album 2, document 311).

ii) There were no illustrations of the vis tellurique in de Chancourtois' Comptes rendus papers. This omission was because of the technical difficulty of printing the charts which de Chancourtois had submitted to the Paris Academy. Although de Chancourtois' pamphlet of 1863 contained illustrations of his system, this publication was not widely circulated.

iii) A model of the vis tellurique made according to the instructions laid down by de Chancourtois would be inconveniently long in relation to its diameter (the charts presented by de Chancourtois himself to the Academy in 1862 were about 5 feet long).

iv) De Chancourtois' inclusion of radicals in a classificatory system of elements probably reduced the acceptability of the system in the eyes of some chemists.

v) Similarly, the inclusion of "secondary characteristics", such as a form of carbon with a "characteristic number" of 44, would probably also have served to discredit the system.

vi) The more important relationships manifested in the vis tellurique (such as the periodicity of properties of the elements) were to a large extent hidden in de Chancourtois' articles among the great profusion of geometrical relationships and numerological speculations.

vii) Some chemists may have been sceptical about the contribution of a geologist to their field; and any such scepticism was in fact vindicated to a certain extent. The manifestations of isomorphism among the feldspars and pyroxenes led de Chancourtois to search for a system of classification which would bring out a simple relationship between the constituent elements of these minerals. Consequently, he suggested the adoption of a "characteristic number" of 55 for Al, which would bring this element onto the same generator of his cylinder as Na and K (see n.92 above). From the chemical point of view, classification of aluminium with the alkali metals could serve only to discredit de Chancourtois' system.

b) Newlands

i) The musical analogy inherent in the term "law of octaves" may have suggested to some chemists an air of wild speculation.

ii) The lack of gaps for possible undiscovered elements in Newlands' tables of 1865-6 was considered a defect of these systems (e.g. by Gladstone, 1866 - see Ch.III, pp.138-9).

iii) Newlands' 1865 and 1866 tables had clear defects from the point of view of chemical analogy. For example, in the third column Cr and Mn were separated, Ti being placed between them (see Figs. III-4 and III-5; this separation of Cr and Mn was condemned by Foster, 1866 - see

Ch.III, p.139); and some of the horizontal rows contained not only the members of a given recognised chemical family, but also elements of quite different properties, e.g. the 6th row contained not only N, P and As, but also Mn (this latter obstacle to the general acceptance of Newlands' "law of octaves" was noted by Mendeleev in his Faraday lecture, 1889[138]).

iv) Although we now see in Newlands' ordinal numbers of the elements something of an anticipation of the modern idea of "atomic number", and tend to consider his abandonment of actual atomic-weight values and differences as displaying foresight (see above, pp.487-9), it is likely that some of his contemporaries were inclined to dismiss his work for the very reason that he did neglect these values and differences.

v) Newlands' presentation of his ideas was possibly too brief, and not clear enough.

c) Odling

i) Odling's publications of the 1860's on the classification of the elements were few, and except for his 1864 paper very brief.

ii) Odling's 1864 paper was published in a relatively obscure journal (Quarterly Journal of Science).

iii) There was a retrogressive character to the series of classificatory systems published by Odling during the period 1864-70: his 1865 tables were in certain respects not as satisfactory as his 1864 table (e.g. as regards the placing of Au; and, in the case of Fig. III-8, because of the omission of Th), and the (no longer "periodic") classificatory system based upon usual valency which was given in his Outlines of Chemistry, 1870, was appreciably cruder than his 1865 tables.[139]

d) Hinrichs

i) The Atomechanik was published as a lithographed reproduction of a manuscript, and was therefore considerably less attractive to the reader than if it had been printed.

ii) Hinrichs' contributions of 1869 were published in American journals, and hence were probably largely unknown in Europe.

iii) Hinrichs' idiosyncratic terminology would have been daunting, and possibly even annoying, to many readers.

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[138] PLBA, 213. Here, and also later in his references to Newlands' work (e.g. see Pr.Ch., R-8, 1906, p.613; PLBA, 314), Mendeleev mistakenly takes the "octaves" as being the horizontal rows in Newlands' tables.

[139] The inferiority of Odling's 1870 classificatory system compared with the system he had included in his Course of Practical Chemistry, 1865, was noted by Mendeleev on p.349 of his article Zur Frage über das System der Elemente, Berichte, 4 (1871) 348-52.

iv) Hinrichs' emphasis on his philosophical ideas (e.g., regarding the arrangement of the ultimate "panatoms") would have tended to create an unfavourable impression among a scientific readership.

v) Apart from the furtherance of his philosophical ideas, Hinrichs' classificatory systems seemed to serve no particular purpose.

Mendeleev's contributions of 1869-71 to the emergence of the periodic law had very little initial impact upon the scientific community within Russia, where most chemists at the time were working in the field of organic chemistry. An exception to this pattern of little response was provided by F.N. Savchenkov, a mining engineer based in St. Petersburg who was very interested in chemistry and its history. On 29th May (O.S.; 10th June, N.S.) 1871 there appeared in the St. Petersburg Gornyi Zhurnal (Mining Journal) a review article by Savchenkov entitled Relationships between the atomic weights of the elements (R.).[140] This was predominantly a factual summary of the contents of Mendeleev's articles Correlation of properties (R.; 1869) and A natural system of the elements (R.; 1871), but there were a few words of appraisal towards the end:

> The future will show the degree of truth of D.I. Mendeleev's suppositions about the existence and properties of elements which are as yet undiscovered;[141] but his assumed natural system of the elements has, in our opinion, a huge significance at the present time for the grouping together of known chemical facts on the basis of the successive change in properties which accompanies change in the atomic weight of the simple bodies. In foreign chemical literature claims are heard on the deductions which have been made by Mr. Mendeleev.[142] An impartial assessment will in time give everyone his due; but it seems that in these claims we can see that Mr. Mendeleev has made a generalisation of an extent attained by no-one else, and we can only be glad that this has been done by a Russian chemist.[143]

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[140] Otnosheniia mezhdu atomnymi vesami elementov, Gornyi zhurnal, 1871, part II, no. 5, pp.234-51 (reprinted in Sc.Ar., 749-61).

[141] This is a reference to the predictions made by Mendeleev in his article A natural system of the elements (R.).

[142] Savchenkov does not cite any specific cases of such priority claims, but he probably has in mind claims by Lothar Meyer (on behalf of himself) and Gerstl (on behalf of Odling) which had been mentioned by Mendeleev in his article Zur Frage über das system der Elemente (publ. April 1871) (see below).

[143] Op.cit., p.250 (Sc.Ar., 760).

Outside Russia the initial response to Mendeleev's work of 1869-71 on the periodic law was greater than it was inside Russia, although it was still no more than moderate. Direct knowledge outside Russia of the content of Mendeleev's Russian-language publications was negligible, acquaintance with his work coming instead from those printed copies of his first periodic table (his "attempt at a system", table 8, headed in French[144]) which Mendeleev himself had sent to various foreign chemists in March 1869, from the German version of this table which was published later in the same month,[145] from a few (inadequate, and even misleading) abstracts in foreign journals[146], from references to his work by certain other authors in German articles[147], and in 1871 from German-language publications by Mendeleev himself.[148]

In connection with the discovery of the periodic system and periodic law there soon appeared a number of comments, claims and disputes concerning questions of priority. By the mid-1880's priority in various respects relating to this field had been claimed for himself by Newlands, Lothar Meyer and Mendeleev, and claims had been made on behalf of Odling by Gerstl. Odling did not claim priority for himself, nor did de Chancourtois. Certain belated claims were made on behalf of de Chancourtois by Hartog (1889: Bibl.26, and by de Boisbaudran and de Lapparent (1891: see Ch.III, n.110). (Concerning Hinrichs' attitude, see n.68 of the present chapter).

Referring to Lothar Meyer's publication of March 1870 (Bibl.81) very shortly after its appearance, Mendeleev acknowledged that "the deductions [sc. concerning the periodicity of properties of the elements] have gained in clarity from the graphical presentation included with this article [sc. Meyer's atomic-volume curve, Fig. III-15]", but he did not acknowledge any

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[144] Essai d'une système des éléments d'après leurs poids atomiques et fonctions chimiques.

[145] Versuche eines Systems der Elemente nach ihren Atomgewichten und chemischen Functionen, J.für prakt. Chem. [1], 106 (1869) 251.

[146] The first such abstracts to appear were the two German abstracts of 1869 discussed in Ch.III, pp.169-70 and 171-2. An English version of the second of these abstracts appeared as Atomic weights, Chem. News, 20, no.524, 10th Dec.1869, p.286. Abstracts of Mendeleev's 1871 publications had appeared by the end of 1871 in German, English and Italian (see Bibl.2, pp.205-41).

[147] Lothar Meyer, 1870 (Bibl.81); C.W. Blomstrand, Berichte, 3 (1870) 539; H. Baumhauer, 1870 (see Ch.V, p.292); R. Gerstl, Berichte, 4 (1871) 132, 484.

[148] Über die Stellung des Ceriums im System der Elemente (see Ch.III, p.172); Zur Frage über das System der Elemente (see Ch.III, p.175); Die periodische Gesetzmässigkeit der chemischen Elemente (see Ch.III, p.175).

other advances in this article over his own work (such as, for example, Meyer's suggestion that indium should be placed in the B-Al group of the periodic system as In = 113.4).[149] It seems a little ironic that Mendeleev should also remark here that "I have no desire to raise the question of scientific priority (in my opinion these questions have no scientific interest)", when it was he more than anyone (except possibly Newlands) who during the subsequent decade or so was to become involved in discussions of priority in connection with the discovery of the periodic law. In this respect we note particularly two papers by him: Zur Frage über das System der Elemente (1871)[150], and Zur Geschichte des periodischen Gesetzes (1880).[151]

The reason for Mendeleev's writing Zur Frage über das System der Elemente (1871), and for publishing it in German, is indicated in the first paragraph of this article: "Because the remarks of Messrs. Gerstl, Blomstrand, Lothar Meyer and Baumhauer concerning the system of the elements proposed by me were made on the basis of incomplete abstracts of my detailed articles which were published in Russian, I shall venture to add some clarification".[152] Mendeleev goes on to express the view that, "It seems to me that the most important distinction between my system and the system of my predecessors consists in my bringing together dissimilar elements".[153] This is a rather surprising remark: apart from the systems of de Chancourtois, Newlands and Hinrichs, of which Mendeleev was at the time apparently still unaware, a "bringing together" of dissimilar elements is certainly evident in a number of the earlier contributions of which he was aware - Odling's 1865 systems, Meyer's 1864 classification, and even some of the work which had been carried

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[149] See Ch.III, p.171.

[150] See Ch.III, p.175. An English abstract of this paper was published under the heading Contribution to the question on the system of the elements in Chem. News, 23, no. 600, 26th May 1871, p.252. A Russian translation of the full paper is given in PLBA, 386-91.

[151] Berichte, 13 (1880) 1796-1804. An English abstract was published under the heading On the history of the periodic law, Chem. News, 43, no. 1103, 14th January 1881, p.15. A Russian version of the full paper is given in PLBA, 396-406.

[152] Op.cit., p.348 (PLBA, 386). Mendeleev is referring to: Gerstl, Berichte, 4 (1871) 132 (priority claim on behalf of Odling); Blomstrand, Berichte, 3 (1870) 533-9 (attempt to classify the elements into two large groups according to odd or even valency, cf. Mendeleev's manuscript table 7); Lothar Meyer, 1870 (Bibl.81); Baumhauer, 1870 (spiral classification of the elements - see Ch.V, p.292).

[153] Op.cit., p.350 (PLBA, 388) (cf. the passage with which Mendeleev concluded Correlation of properties, 1869, quoted in Ch.III, p.169).

out during the 1850's, such as that of Kremers and Lenssen. Later in this article of 1871, in reference to Lothar Meyer's comment of 1870 that "already in 1864 I was able to bring regularities found in different families of chemical elements under one and the same scheme",[154] Mendeleev wrote, "one only has to read the cited source [sc. Bibl.80, 1864] to be convinced that Mr. Meyer in 1864 did not devote himself to an account of those relationships among the elements which I have advanced; strictly speaking, he merely presented a simple collocation of groups of analogous elements".[155] Near the end of Zur Frage über das System der Elemente Mendeleev again (as in 1870) protested his aversion to priority considerations, at the same time however defending his own priority claims:

> Although I am an opponent of all questions of priority I have nevertheless decided to make these remarks, particularly since Gerstl, Meyer, and to some extent Blomstrand contend priority of my system, but do not come out against each other with such claims - although claims against each other would have been more just, in view of the dates of appearance of the above-mentioned articles. The enumeration of such various claims is already in itself sufficient to show that my deductions serve to answer problems which were posed by the above-mentioned prominent chemists, while not being at the same time repetitions of their statements. I think also that it may be suggested that after a detailed acquaintance with the results obtained by me, the independence of my ideas will not be disputed.[156]

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[154] Bibl.81 (see Bibl.67, p.10).

[155] Op.cit., pp.351-2 (PLBA, 390). The unjustness of Mendeleev's dismissal of Meyer's 1864 classification is pointed out earlier in the present chapter, on p.481.

[156] Op.cit., p.352 (PLBA, 390). Gerstl had claimed priority for Odling's 1865 system, a claim which Mendeleev failed to answer satisfactorily. Gerstl responded to Zur Frage über das System der Elemente by repeating his claim on behalf of Odling (Berichte, 4, p.484, 4th May 1871). Mendeleev did not reply to this; in fact, he seems never to have referred again to Odling's contributions of the 1860's. As regards Meyer and Blomstrand, there was little if any justification for Mendeleev's assertion in Zur Frage über das System der Elemente that these scientists had contended priority with him over the periodic system. Meyer in 1870 had referred only in very general terms to "regularities" which had been manifested in his 1864 classificatory scheme (see above); and at the same time he had even acknowledged that his new system of 1870 was "essentially identical to that given by Mendeleev" (see Ch.III, p.152). Blomstrand's reference to Mendeleev had been merely to remark that "Mendeleev has drawn attention to the known relationships of the atomic weights from another point of view" (Berichte, 3, p.539, 1st June 1870).

During the period 1871-5 the periodic law attracted relatively little attention, despite the corroboration of many of the atomic-weight changes proposed by Meyer (for In) and Mendeleev (for In, U, Ce, etc.) on the basis of the law. By 1872 even Meyer and Mendeleev themselves had largely turned their attention to other fields. Claims of priority in discovering the periodic law were published by Newlands in 1872 and 1873[157]; but it was not until after the discovery of gallium by de Boisbaudran in 1875 that the periodic law began to gain widespread appreciation. The properties determined for gallium during 1875-6 provided striking confirmation of Mendeleev's predictions of 1870-1, on the basis of the periodic law, of the existence and properties of "eka-aluminium".[158] It was Mendeleev himself who drew attention to the identity of de Boisbaudran's gallium with his own predicted "eka-aluminium", in a note to the Comptes Rendus in 1875.[159] In addition to pointing out the confirmation of his predictions for "eka-aluminium", and emphasising the general applicability of the periodic law for predicting the existence and properties of unknown elements, Mendeleev in this communication drew attention also to two other important aspects of the periodic law - viz. the fact that a single classificatory system for all elements can be based upon it, and the fact that it can be used for determining the atomic-weight values of known elements. In connection with the latter use Mendeleev listed the changes he had proposed on the basis of the periodic law for the atomic-weight values of In, U, Ce, Th, Y, Er, Di and La (he did not mention Lothar Meyer's contribution in connection with the atomic weight of indium), and referred to the evidence which had subsequently been obtained in support of these proposals. In 1877 the 3rd edition of Mendeleev's Principles of Chemistry (R.) was published; this was the first edition of this work to contain a special chapter devoted to the periodic law. In 1879 scandium was discovered, and shown to correspond to Mendeleev's "eka-boron".[160] Because of "considerable attention have been drawn to M. Mendeleef's memoir 'On the Periodic Law of the Chemical Elements' [sc. Die periodische Gesetzmässigkeit der chemischen Elemente, Annalen, 1871], in consequence of the newly discovered elements gallium and scandium being

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[157] Chem. News, 25 (1872) 252; 26 (1872) 19; 27 (1873) 318.

[158] See Ch. VI, pp. 354-68.

[159] See Ch. VI, n.113 (p.354).

[160] See Ch. VI, pp. 355-67.

apparently identical with his two predicted elements ekaluminium and ekaboron",[161] this article was republished in English translation in the Chemical News of 1879-80.[162]

The year 1880 saw a priority dispute concerning various aspects of the discovery of the periodic law between Mendeleev and Lothar Meyer, in the German journal Berichte; and although this dispute was of no great credit to either scientist personally (especially Mendeleev), it added further to the publicity of the periodic law. The fact that it had been confirmation of Mendeleev's predictions for "eka-aluminium" and "eka-boron" that had originally stimulated widespread awareness and appreciation of the periodic law had led, quite understandably, to a general acknowledgment of Mendeleev as discoverer of the law, the contributions which had been made by others in connection with the periodicity of properties of the elements tending to be somewhat eclipsed by his work. Hence the publication by Lothar Meyer in 1880 of a paper Zur Geschichte der periodischen Atomistik[163], written "in order that his share in the matter may not be forgotten".[164] Meyer in this article was reasonably fair in his comments upon those contributions of Mendeleev's of which he was aware and in his comparison of these contributions with his own, but his lack of knowledge of the detailed content of Mendeleev's original Russian articles of 1869-70 led him to accuse Mendeleev unjustifiably of adopting without acknowledgment various ideas and results which had been presented by Meyer himself in 1870 (such an accusation seems to be justified, however, for the particular case of the atomic-weight value of indium). This prompted a reply from Mendeleev in the form of his article Zur Geschichte des periodischen Gesetzes.[165] Here Mendeleev quoted extensively from his early Russian articles on the periodic law, adding a number of comments in footnotes; he then concluded,

> From these extracts (and from the notes I have made on them) it is clear: 1) that in my articles of March and August 1869 I included all those ideas which up to the present day constitute

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[161] Chem. News, 40 (1879) 231.

[162] See Ch.II, n.156, i).

[163] Berichte, 13 (1880) 259-65. A slightly abridged English version was given as On the history of atomistic periodicity in Chem. News, 41 (1880) 203. This paper of 1880 was used by Meyer to make a belated reply to Mendeleev's Zur Frage über das System der Elemente, 1871 (see n.51 of the present chapter).

[164] See Chem. News, 41 (1880) 203.

[165] See above, n.151.

the basis of the periodic law; 2) that Lothar Meyer did not think of the periodic law before I did, and afterwards added nothing new to it; 3) that Lothar Meyer was the first German chemist to understand the external aspects of my ideas concerning the periodic law and 4) that he did not however understand the inner significance after the appearance of my first article (1869), because although he also afterwards published an article (1870 in Liebig's Annalen Suppl. VII), he only repeated in another form what had already been developed by me before him, and he did not develop those aspects of the subject (composition of oxides, prediction of properties of unknown elements, change of atomic weights of Ce, Yt, Ur, etc.[166]) which alone can convince of the truth and generality of the law. I had to develop these aspects myself, which I did in 1870-1871. I had already made a preliminary reference to these aspects in my original article of March 1869.

If anything new had been added in the development of the study of the periodic law, then this has been done by Th. Carnelley (Berichte XII, p.440; Phil. Mag., Oct., Nov., Dec., 1879), who has shown that the melting-point and magnetic properties stand in periodic dependence upon atomic weight.

I consider it necessary to add to what has been said above that the English journals (e.g. Phil. Mag., 1869,[167] Oct., p.310) maintain that Mr. Newlands in 1864 ... presented, before I did, a law like the periodic law.[168] I did not see this publication, and have so far been unable to get hold of it ...[169] Maybe Newlands ... did express a law like the periodic law before I did, but even this cannot be said of Lothar Meyer ... But to Newlands, just as to Meyer, the present state of the question of periodicity owes nothing.

In order to make my thoughts on priority questions completely clear, I add that I have become involved in this affair only because Mr. Meyer chose in his article (Berichte XIII, 263) to express the thought that I had taken something from him in my development of the periodic law.[170]

Shortly afterwards, Meyer published a brief reply,[171] pointing out that he could hardly be expected to read Russian, and that he still felt

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[166] It is interesting that Mendeleev does not specifically mention indium here.

[167] "1869" here is a mistake for "1879".

[168] Lothar Meyer (Berichte, 13, 1880, p.261) had already mentioned the possibility that Newlands might have some claim to priority in connection with the discovery of the periodic law.

[169] Part of the section omitted here is the passage quoted earlier in the present chapter on p.482.

[170] Op.cit., pp. 1801-3 (PLBA, 403-5; see also Chem. News, 43, 1881, p.15).

[171] Zur Geschichte der periodischen Atomistik, Berichte, 13 (1880) 2043-4. Published in English translation as The history of atomic periodicity, Chem. News, 43 (1881) 15.

that Mendeleev should have referred to him in his article of 1871 in Liebig's Annalen. He concluded: "No one probably has taken such pains to secure for the results of H. Mendelejeff's researches universal diffusion and recognition as I have done in the three editions of my 'Modern Theories of Chemistry', which have since appeared".[172]

In 1882 the Royal Society recognised the importance of the periodic law, awarding the Davy Medal for its discovery to both Mendeleev and Lothar Meyer. Five years later Newlands also was awarded the Davy Medal for his part in the discovery of the periodic law; the Royal Society had probably been to some extent persuaded into this by the case presented in support of his own priority by Newlands in his booklet of 1884 On the discovery of the periodic law and on relations among atomic weights (Bibl.84).

In 1886 further corroboration of the periodic law was provided by Winkler's discovery of germanium, confirming Mendeleev's prediction of "eka-silicon".[173]

In 1877 the attention of the Czech chemist Brauner had been attracted to the periodic law, particularly to Mendeleev's exposition of it in The periodic lawfulness of the chemical elements (G.; 1871).[174] Brauner soon became so convinced of the fundamental importance of the periodic law for chemistry that most of his work from the late 1870's on was devoted to the consolidation of the law.[175] Although the late 1870's and the 1880's certainly saw the widespread recognition and acceptance of the periodic law, with progressive consolidation of the law as Mendeleev's "eka"-predictions came to be confirmed and as the atomic-weight values of certain elements (e.g. U, Be) became increasingly convincingly shown to correspond to those demanded on the basis of the law, not many scientists accepted the periodic law with such firm conviction as Brauner. In fact, Brauner's faith in the periodic law seems to have been surpassed only by that of Mendeleev; even Lothar Meyer and Newlands, while being staunch champions of the periodic law do not appear to have been quite as committed as Brauner

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[172] Chem. News, 43 (1881) 15.

[173] See Ch. VI, pp. 355-67.

[174] See Ch. VII, p.424.

[175] See pp. 330 (concerning Be), 341 (Ce), 344-6 (Te) and 423-35 (rare-earth elements). A survey of Brauner's contributions in connection with the periodic law is given by Kedrov in Bibl. 38, pp. 73-112.

to belief in its general validity and applicability.[176] A common attitude towards the periodic law by the mid-1880's was one of slightly qualified support, i.e. acknowledgment of the many advantages of the periodic law and periodic system as presented by Mendeleev and Meyer, while at the same time recognising certain inadequacies. Those whose support for the law, within this pattern, was particularly strong included the English scientists Carnelley, Roscoe and Crookes. Wurtz also showed considerable support for the periodic law.[177] Ostwald acknowledged the law as having much in its favour, but at the same time saw in it a number of weaknesses. Thus, in 1885 he published the following remarks:

> The numerous and unexpected developments which the Periodic Law has given us as to the relations of the atoms, one to another, should not make us blind to certain difficulties which have arisen in its full application. Thus the discussion over the atomic weight of beryllium is not yet closed...[178] Again, elements are separated from one another which in the form of their compounds stand close together - as mercury and copper, with which it has more points of resemblance than with zinc and cadmium. Sodium is separated from the alkali metals proper and placed with copper, silver and gold. The silver here shows, at best, a relationship through the isomorphism of the water-free sulphate. Also the oxidation steps held up by Mendeléeff as characteristic or typical are neither the only ones, nor the lowest, nor yet the highest, indeed they are often unknown and incapable of existence.
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> These objections are not raised to refute the Periodic Law. They are too few in number for that and stand opposed to too many favoring circumstances. They serve only to show that the law in its present form is only the beginning of a most promising line of thought.[179]

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[176] Thus, Meyer in 1880 (Berichte, 13, p.265; Chem. News, 41, p.203) referred to Mendeleev's correct prediction in 1870-1 of the properties of the then unknown gallium and scandium as "fortunate", which suggests that he still retained some of the uncertainty he had shown earlier (Bibl.81, 1870) regarding the use of the periodic system for prediction; and Newlands in 1884 remarked, "Although all the elements yet discovered appear to take their places in accordance with the periodic law, it is quite conceivable that various series of elements may exist not very simply related to each other" (Bibl.84, p.36). It should be noted at the same time, however, that Brauner himself as early as 1882 acknowledged (albeit privately, in a letter to Mendeleev) that perhaps there exist "anomalies" in the region of the periodic system between Ba and Ta (see Ch.VII, p.430).

[177] In a manuscript of 1899 (see Bibl.70, p.55; Colls., 25, 701) Mendeleev was to write, "From my side, I consider that Wurtz contributed greatly to the popularisation of my system of the elements", referring particularly to Bibl.132 (and its later editions and translations).

[178] At about this very time the evidence in support of the atomic-weight value Be = 9 rather than Be = 14 was in fact becoming overwhelming (see Ch. VI, pp. 330-1).

[179] Lehrbuch der Allgemeinen Chemie, 1885, pp.126-7. The English translation given here is from Venable, Bibl.124, pp. 115-7.

Apart from Ostwald's remarks here concerning the "oxidation steps held up by Mendeleeff as characteristic or typical", which were largely unjustified and which indicated a lack of appreciation of Mendeleev's recognition of these "oxidation steps" as those of the highest "saline" oxides,[180] this passage represents a very fair appraisal of Mendeleev's periodic classification of the elements relative to the state of chemistry at the time.

A few prominent chemists remained sceptical of the periodic system, or even ignored it. Bunsen seems to have ignored it; and Berthelot in his Les Origines de l'Alchimie (1885) was very sceptical of its value, although this scepticism was founded mainly upon misrepresentation and misconception of the periodic law. Berthelot's claim that the periodic system indicates that "between S = 32 and Se = 79 there should exist two intermediate terms 48 and 64"[181] shows his misunderstanding of the system.

With the growing problem of the rare-earth elements, and with the discovery of the inert gases, doubts about the universal usefulness and validity of the periodic system tended to increase during the 1890's. More scientists came to show Ostwald's attitude of 1885, treating the periodic law as a good "first approximation". Venable, for example, wrote of the periodic system in 1896, "Its imperfections are many, but they are outweighed by its virtues and the truths which it so well presents. That there can be a better presentation of them is most likely".[182] More critical than most at this time was Wyrouboff, who felt that Mendeleev's periodic classification showed an "arbitrary selection of oxides and of atomic weights" (1896).[183]

1900 saw the satisfactory placing of the inert gases in the periodic system in a new "zero" group, strengthening confidence in the system. But whereas the periodic system thus convincingly incorporated the inert-gas elements, it failed to stand up to the challenge of the lanthanides in anything like the same way. Brauner in 1901 presented his "asteroid" solution to the problem, assigning cerium and all of the heavier rare-earth elements a single place in group IV of the system, immediately following

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[180] See Ch.V, pp. 309-10.

[181] Les Origines de l'Alchimie, 1885, pp. 308-14 (see Venable, Bibl.124, pp. 110-114).

[182] Bibl.124, p.10.

[183] Chem. News, 74 (1896) 31. (See Ch. V, pp. 309-10).

lanthanum in group III.[184] This solution was not generally adopted. Mendeleev, for example, although a great admirer of Brauner's work in the field of rare-earth chemistry, did not adopt it.[185] Although to the end of his life Mendeleev preferred to regard the problem of the lanthanides as an "open question", he was nevertheless eventually forced to acknowledge the possibility that the periodic system "shows a break in its form" in the atomic-weight region 140 - 183.[186] With the theoretical consolidation of the periodic system between 1910 and 1915 as a result of the work particularly of Rutherford, Bohr and Moseley[187], and with the subsequent emergence of the quantum-mechanical interpretation of the electronic states available to the atom, the lanthanide elements (and, subsequently and similarly also the actinides) have turned out to provide a weak refutation of the periodic law as viewed by Mendeleev, to represent indeed "a break in the form" of the periodic system.[188]

The shift of the basis of the periodic system from that of atomic-weight ordering to that of atomic-number ordering which followed Moseley's results removed the earlier problem of the atomic-weight inversions of Te - I, Ar - K and Co - Ni in the system.

The significance of the periodic system for chemistry can be recognised in various respects:-

i) Ontological significance (i.e. significance for the fundamental structure of chemistry).

The periodic system provides a stable and coherent definitive framework for chemistry. Prior to the discovery of the periodic system the criterion for the recognition of a chemical element was in terms solely of the "negative operational" definition of a simple substance (free element) as a limit of analysis, the recognition of any particular substance as being

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[184] See Ch. VII, pp.430-2.

[185] See Ch. VII, pp. 431, 433.

[186] See Ch. VII, pp. 433-4.

[187] These contributions of Rutherford, Bohr and Moseley, and related contributions by other workers, are chronicled in PLBA, 798-801, and in Bibl. 109.

[188] The weak refutation of the periodic law provided by the lanthanide elements may be contrasted with the weak corroboration of Bode's law of planetary distances in the solar system provided by the asteroid belt.

an element thus being dependent upon the stage of development of experimental analytical techniques and knowledge of spontaneous decomposition processes. But with the discovery of the periodic system a permanent (stable) criterion was introduced for the recognition of any particular element - viz. occupancy of a place in the system - and a single coherent system for all elements was provided: chemistry was now no longer the science which sought the ultimate structure of matter, but instead the study of a certain intermediate level of matter, viz. the study of the chemical elements.[189]

ii) Epistemological significance for the concept of "element".

The periodic system provided consolidation of the long-standing tacit assumption by most chemists that the chemical elements persist in some real (though "transcendental") sense throughout chemical change.[190] As Mendeleev emphasised, "The various periodic relations belong to the elements, not to the simple bodies, and this is extremely important to note".[191]

iii) Scientific significance.

The structure of the periodic system and the analogies and trends manifested in the system have provided a basis for the prediction of the existence and properties of elements, and, conversely, a basis for explanation at a corresponding level (i.e. in terms of the structure of the system and the analogies and trends within it) of the existence and properties of elements. Also, as a single coherent classificatory system embracing all elements the periodic system by its very nature strongly indicates (and, historically, has indicated to many scientists[192]) the existence of a genetic link between the elements. Further, the periodic classification of the elements has led to a consolidation and sharpening of the concept of valency in various respects, e.g. in Mendeleev's identification of group-number in the periodic system with maximum valency in "saline"

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[189] Thus, Mendeleev wrote in 1871: "the entire doctrine of chemistry is the doctrine of the properties of the elements" (see Ch.I, p.28). More recently F.A. Paneth has written, "Even today chemistry is the theory of the chemical elements" (1934; see Bibl. 90, p.70), and J.W. van Spronsen has remarked that "... chemistry has grown into a closed system (in the logical sense of the term) ..." (1969: Bibl.110, p.2).

[190] See Ch. I, especially pp. 27, 28, 31 and 33-4.

[191] Pr.Ch., R-8 (1906) 620 (PLBA, 327).

[192] See Ch. II, pp. 76-7 and 102-5.

oxides, and in his (and later Abegg's) discovery of the "rule of 8" regarding the relationship between valency in saline oxides and valency in volatile hydrides.[193]

iv) Pedagogical significance.

The periodic system provides a compact expression of the diverse chemical and physical relationships among the elements, and as such is of great pedagogical significance. Mendeleev's Osnovy Khimii (Bibl.65; from 1869) and Lothar Meyer's Die modernen Theorien der Chemie (Bibl.80; from 1872) were the first of many textbooks of general and inorganic chemistry to be based upon the periodic system; and even before Meyer and Mendeleev had constructed their periodic systems Odling had already given his similar system of 1865 a pedagogical application.[194] In 1871 Mendeleev wrote that "the systematic exposition of the facts of chemistry for beginners is very much improved by basing this on the periodic law".[195] Venable, 25 years later, had the following to say on the subject of classificatory tables based upon the periodic law: "The discovery of scandium and gallium and their fitting into the predicted places ... gave a new impetus to the study of these [periodic] tables and their use in the classroom".[196] The organisation of most modern textbooks of inorganic chemistry is based upon the periodic system.[197]

As a result of the consolidation of the periodic system during the present century and the accompanying clearer recognition of chemistry as an intermediate-level study of matter (viz. as the study of the chemical elements), the fundamental significance for chemistry of the discovery of the periodicity of the elements is now even more evident than it was during Mendeleev's lifetime. In view of this fundamental significance (in all four

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[193] See n.132 of the present chapter.

[194] Thus, one version of Odling's 1865 table appeared in his Course of Practical Chemistry (see Fig. III-8), and one in Watts' Dictionary of Chemistry (see Fig.III-7).

[195] The periodic lawfulness of the chemical elements (G.), Annalen, 1871, p.171 (PLBA, 131).

[196] Bibl.124, p.9. My underlining.

[197] A fairly recent textbook of inorganic chemistry which shows particular dedication to the use of the periodic system as the framework for presentation of the physical and chemical properties of the elements is Sanderson's Chemical Periodicity, 1960 (Bibl.102).

of the senses considered above, but especially the "ontological", "epistemological" and "scientific", since it is from these that the "pedagogical" significance arises) it seems not unreasonable to recognise the discovery of the periodicity of the elements as being the most important development in 19th-century chemistry. The primary importance here lies in "public" discovery by the scientific community, not in "private" discovery by a particular scientist;[198] and it was Mendeleev's contribution which played by far the major role in leading to the awareness and appreciation of the periodic law by the scientific community in general - a consequence of his clear perception of the importance of the law, the detail and extent of his discussion of it, the boldness of his use of it for prediction, and his dedication to its promotion. This is a recognition of the primacy of Mendeleev's involvement in establishing the basis for the "public" discovery of the periodic law; it is not a claim of his priority as regards "private" discovery of the law. The bare "private" achievement of independent construction of a prototype periodic system can be seen in the work not only of Mendeleev but also of de Chancourtois, Newlands, Odling, Hinrichs and Lothar Meyer.[199]

In 1889 the English chemist T.E. Thorpe wrote of Mendeleev that "he has become to Russia what Berzelius was to Sweden, or Liebig to Germany, or Dumas to France".[200] From the present-day perspective, and with the recognition that simple ranking according to merit of different contributions to the development of science tends to beg so many questions that it often has little historiographical significance apart from stimulating discussion and debate, the following conclusion is presented: taking the discovery of the periodic law to be the most important development in 19th-century chemistry, and taking Mendeleev's role in this discovery to be pre-eminent, we remove such restrictions of national boundary as are imposed in the above-quoted judgment by Thorpe and suggest that Mendeleev should be acknowledged as the most important of all chemists of the 19th century.

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[198] See earlier in the present chapter, p.482.

[199] See earlier in the present chapter, pp.479-82.

[200] Bibl.113, p.197.

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